The fate and impact of fertiliser derived contaminants in New Zealand soils – development of a priority assessment model

Von der

Fakultät Architektur, Bauingenieurwesen und Umweltwissenschaften

der Technischen Universität Carolo-Wilhelmina

zu Braunschweig

zur Erlangung des Grades eines

Doktors der Naturwissenschaften (Dr. rer. nat.)

genehmigte

Dissertation

von Matthew David Taylor
geboren am 6. Dezember1961
aus Auckland, New Zealand

Eingereicht am: 29. Februar 2016

Disputation am: 21. November 2016

Berichterstatter: Prof. Nieder
Prof. Biester
Prof. Schnug
Prof. Durner

(2016)

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Publications resulting from this work:

1. Taylor MD, Lowe DJ, Hardi P, Smidt GA, Schnug E. (2016) Comparing volcanic glass shards in unfertilized and fertilized Andisols derived from rhyolitic tephras, New Zealand: evidence for accelerated weathering and implications for land management. Geoderma 271 (2016) 91–98.
2. Taylor MD, Schnug E, Curran-Cournane F, Guinto D, Gray C, Drewry J, Cuff J.R, Briggs R. (2014) Background concentrations of major and trace elements in NZ soils by XRF and acid extraction compared to World literature. New Zealand Soil Science Society conference "Soil science for future generations", Hamilton, New Zealand, December 1-4, 2014.
3. Taylor MD, Kratz S, Schick J, Schnug E, Smidt G (2014) Comparing trace element concentrations in inorganic and organic fertilisers. New Zealand Soil Science Society conference "Soil science for future generations", Hamilton, New Zealand, December 1-4, 2014.
4. Taylor MD, Schnug, E, Curran-Cournane F, Guinto D, Gray C, Drewry Ledgard G, Bedford G, Lynch B, Burton A, Cuff JR, Briggs R (2014) Elemental concentrations in soil under different land uses in NZ. New Zealand Soil Science Society conference "Soil science for future generations", Hamilton, New Zealand, December 1-4, 2014.

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AP	Ammonium phosphates
BF	Blended nitrogen phosphorous potassium fertilisers,
BG	Background
C:Gv	The ratio of trace element concentration in fertiliser to soil guideline value
CMG	Cadmium Management Group
CWG	Cadmium Working Group
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EEZ	Exclusive economic zone
EPA	New Zealand Environmental Protection Authority
F: BG	The ratio of an element in fertiliser to background soil
GWRC	Greater Wellington Regional Council
HBRC	Hawkes Bay Regional Council
IANZ	International accreditation New Zealand
ICP-MS	Inductively coupled plasma mass spectroscopy
ICRP	The International Commission on Radiological Protection
K_d	Partitioning coefficient
M^{2+} cations	Divalent metal cations
MDC	Marlborough District Council
MfE	New Zealand Ministry for the Environment
NZ	New Zealand
RBE	The relative biological effectiveness
RMA	The Resource Management Act 1991
RRE	Rare earth elements
RRP	Reactive Rock Phosphate, which is ground phosphate rock
SOM	Soil Organic Matter

SP	Single superphosphate
Std Dev	Standard Deviation
TF	Soil-plant transfer factor
TOC	Total organic carbon
TRC	Taranaki Regional Council
TSP	Triple superphosphate
XRF	X-ray fluorescence
WRC	Waikato Regional Council

Author's previous publications underpinning this thesis:

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1. Introduction

1.1 Trace elements in fertilisers

Population growth, industrialisation, urbanisation, climate change and wider socio-economic drivers are putting pressure on the sustainability of natural resources such as land, water, and energy (Jarvie et al. 2015). One such pressure is environmental contamination. Although point sources of contamination are now largely managed in NZ, there remain considerable challenges to managing sources of diffuse contamination, including the unintentional application of contaminants of fertilisers.

Fertiliser is applied by thousands of farmers across NZ (Figure 1.1) and in many countries of the world, but fertilisers also contain trace elements as well as the major nutrients. Some of these trace elements are trace nutrients while others are always considered contaminants. They may accumulate in soils (Taylor et al. 1997), river, lake and estuarine sediments (Kim 2005) or transfer to ground or surface waters (CWG 2008), thereby undermining the health of land and aquatic ecosystems and jeopardising food and water security.

Figure 1.1: Aerial application of superphosphate fertiliser in NZ (John Maber. 'Topdressing Commercial developments of aerial topdressing, Te Ara - the Encyclopaedia of New Zealand).

Whether the full scope of the contaminants found in fertilisers has been sufficiently identified is debateable. Trace elements reported in mineral fertilisers include As, Cd, F, Pb, Hg and U (McLaughlin et al. 1996), while a substantial accumulation of Cu from the use of piggery products has been reported (Eriksson 2001, Chang & Page 2000). However, these elements appear often targeted as they have been identified in previous studies.

Some trace elements are added deliberately to overcome deficiency in soils, but these, if inappropriately applied, can build up to toxic levels in the receiving environment. The potential consequence to land, water and the marine environment will depend on the quantity of the trace element applied to land (the fertiliser management regime and the amount of a contaminant applied), its chemical characteristics (particularly sorption and transfer properties), and its level of toxicity to biota. Thus, the use of fertilisers has significant implications including sustaining of the range of existing and foreseeable future uses of land, water and the coast. However, there is a lack of information on current and historical inputs of trace elements from fertilisers to the NZ environment as trace element concentrations are not routinely measured in fertilisers.

Historically, in regulations governing maximum allowable concentrations of trace element contaminants in various environmental compartments, there has been much focus on metals (Molloy et al. 2005). This is understandable as organisms tend to be highly sensitive to metals, which are already widespread in nature and sometimes at concentrations close to critical toxicity threshold levels for organisms. So, in some situations, a relatively small increase above background concentrations for a particular metal may result in adverse human or ecological effects. Metals also tend to be concentrated by the same forces that concentrate P into potential fertiliser sources such as rock phosphate ore deposits or sewage sludges and manures (Molloy et al. 2005).

Other important groups of trace elements are metalloids, lanthanides or rare earth elements, radionuclides and anionic elements. As is the metalloid of most concern due to a combination of its moderately high natural abundance in the environment and toxicity. As is commonly

found in different oxidation states in natural systems and its toxicity to organisms, bioavailability and mobility is controlled by their oxidation state, e.g. As (III) is more toxic than As (V). The anionic element Cr shows similar properties, e.g. Cr (VI) is more toxic than Cr (III) (Molloy et al. 2005).

Lanthanides or rare earth elements (RRE) are elements with atomic numbers 57-71 that, except for promethium (atomic number 61, a short-lived radioisotope), are found naturally in the environment. Molloy et al. (2005) found very little information was available regarding their toxicity and behaviour in the environment.

Radionuclides can be toxic as a result of their chemical properties but they are primarily of concern because they emit radiation that can damage DNA leading to carcinogenic and/or teratogenic impacts (Busby & Schnug 2008, Molloy et al. 2005). Several naturally occurring radionuclides occur in soils including isotopes of K, U, Th and Ra. These are often found at higher concentrations in P rock ores and can be transferred into the fertiliser product.

Anionic elements include the halogens (Group 7A, F, Cl and Br), and the oxyanions (As, Cr, Mo and Se) that combine with oxygen to form stable negatively charged species. The charge on any element or molecule has a large bearing on its behaviour in the environment and biota. Molloy et al. 2005 reported F as the anionic element of greatest concern for vertebrates in agricultural systems due to its toxicity to these organisms and high concentration in mineral P fertilisers. Molloy et al (2005) also noted that high concentrations of Cl can result in toxicity to plant and soil micro-organisms, and since many waste streams can be highly saline, it needs to be ensured that any potential fertiliser made from such streams is not compromised by excessive Cl levels.

As the removal of contaminant trace elements from fertiliser products has not been widely practised, most manufactured mineral P fertilisers, by-products such as phosphogypsum as well as many organic fertilisers may contain appreciable amounts of these trace elements.

The site of dynamic interaction between the atmosphere (both in and above the soil), biosphere, lithosphere and the hydrosphere (water in, on and below the soil) is called the pedosphere or the critical zone of life (Juma 1999). It extends from the top of the vegetation canopy down to and including the zone of freely circulating fresh groundwater and sustains nearly all terrestrial life (Amundson et al. 2007). This critical zone concept is important as it crosses environmental compartments, not simply addressing the soil or water or air, but all of them as a whole. The rapidly expanding needs of society give special urgency to understanding the processes that operate across environmental compartments. The critical zone principle is applied in this study to assess the fate of trace elements applied to land in fertilisers, their possible transfer to water, sediments and the coastal environment.

1.2 The management the environmental resource in NZ

This section outlines the regulatory environment and policy development process in NZ. NZ is an isolated country in the South Pacific (Figure 1.2) and is divided into sixteen regions for local government (Figure 1.3). Regional authorities and New Zealand's Environmental Protection Authority (EPA) are responsible for the management the environmental resource in NZ. The EPA administers applications for major infrastructure projects of national significance, and regulates new organisms (plants, animals, GM organisms), hazardous substances and chemicals. The EPA also administers the Emissions Trading Scheme and New Zealand Emission Unit Register, and manages the environmental impact of activities in the EEZ, including prospecting for petroleum and minerals, seismic surveying and scientific research. Environmental management in all other areas is the responsibility of the regional authorities.

Much of the data underpinning this thesis were collected in the Waikato region, so examples of mangaging the environment in NZ are taken from this region. It has a largely rural economy with dairy, sheep and beef farming, and forestry the major industries. The region has one major city, Hamilton and several rural towns (Figure 1.4). It has one major river, the Waikato. Two smaller rivers, the Piako and Waihou, drain the Hauraki catchment and discharge near Thames.

Figure 1.2: Map of the world with New Zealand in the centre (Nelson City Council).

The Resource Management Act 1991 and its amendments (RMA) is the core piece of legislation controlling how the use of the environment is managed in NZ. A detailed guide to this RMA is provided in Appendix 1.1 and an outline is provided below as it is of such importance in understanding the role of research in the management of the environment in NZ.

The RMA defines ‘contaminated land’, requires planning controls to manage the discharge of hazardous substances and effects of these substances in or on land. Under the RMA, the bulk of decision-making authority rests with local government. So, regional authorities are primarily responsible for environmental management, including water, contaminant discharge and coastal management, river and lake management including flood and drainage control, regional land management; regional transport (including public transport) and harbours, biosecurity or pest management. This responsibility includes managing any adverse effects from the application of fertilisers.

Figure 1.3: Map of NZ showing Regional authority boundaries (imgarcade.com. http://imgarcade.com/1/new-zealand-political-map/).

Research is required to meet the needs of this legislation. A part of the RMA is section 32, which is to ensure rigour in plan decision-making through requiring a critical evaluation of the objectives, policies and methods of proposals.

In addition, regional authorities have a duty under section 35 of the RMA to gather information, monitor and keep records on the efficiency and effectiveness of their policies and rules, e.g. The Waikato Regional Council monitors soil, surface and ground waters, and lake

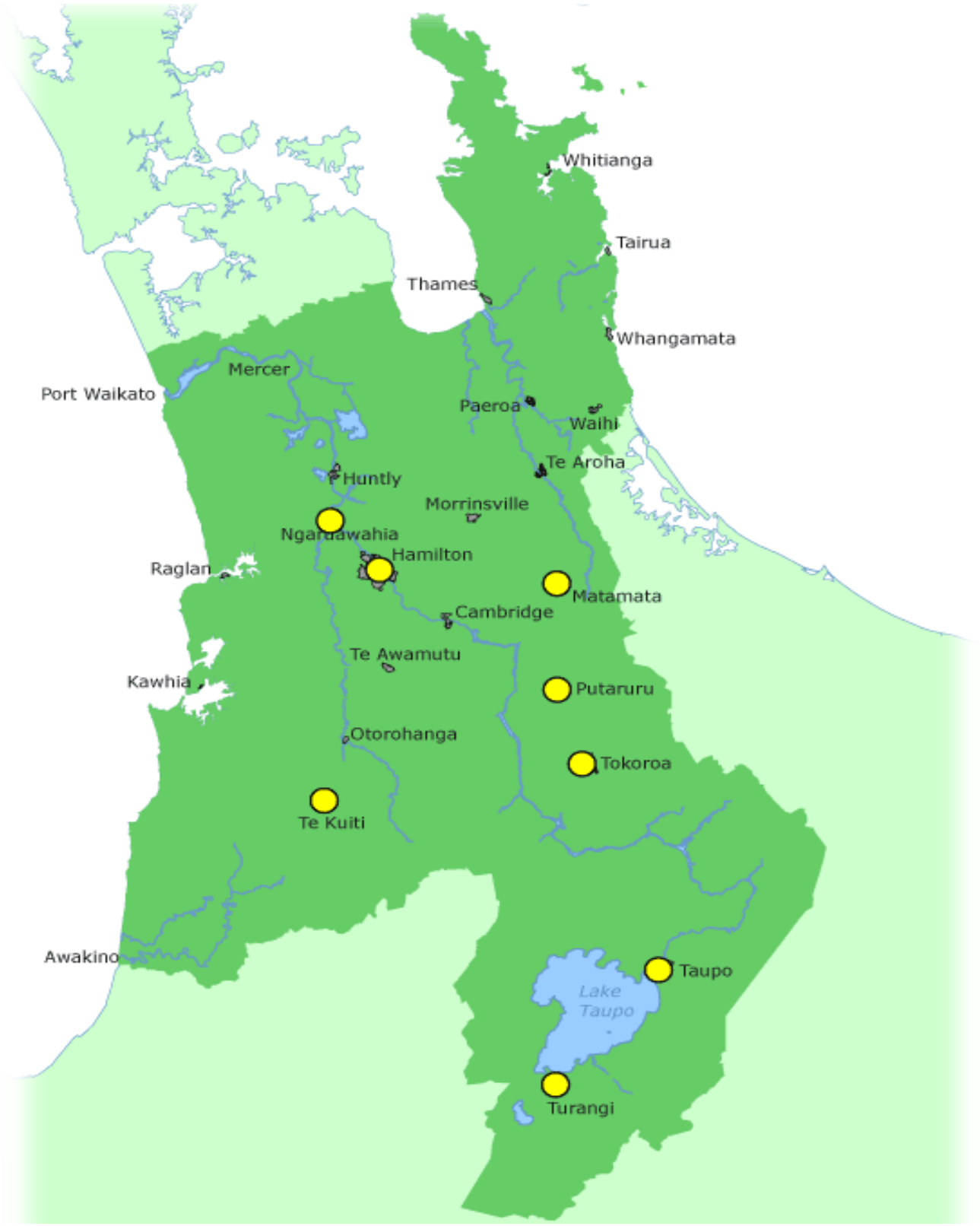

Figure 1.4: Map showing the location of towns and Hamilton City, Waikato, New Zealand (Waikato Regional Council).

and estuarine sediments to assess the effectiveness of these four policies relating to diffuse contamination:

- Policy 8.3 Manage activities to maintain or enhance the values of water bodies
- Policy 11.1 Maintain or enhance indigenous biodiversity
- Policy 14.1 Maintain or enhance the life supporting capacity of the soil resource
- Policy 14.3 Ensure that accumulation of contaminants in soils does not cause a reduction in the range of existing and foreseeable uses of the soil resource.

The critical evaluation prepared for Policy 14.3 shows five policy options were considered:

- Policy option 1: Regulate to ensure no further accumulation for key contaminants in soils.
- Policy option 2: ALARA. Accumulation of key contaminants in soil is kept **A**s **L**ow **A**s **R**easonably **A**chievable.
- Policy option 3: Adopt maximum soil guidelines for key contaminants.
- Policy option 4: Adopt identified ranges for key contaminants, depending on land use.
- Policy option 5: Status quo.

Further, a policy needs methods of how it is to be achieved, e.g. Policy 14.3 above has *implementation method 14.3.1 Control discharges to land* and includes … "*For key soil contaminants including [ie. not restricted to] cadmium, fluorine and zinc, Waikato Regional Council will consider:*
a) adopting risk-based guidelines for contaminants in soil and linking these with specific management actions; and
b) establishing processes to determine discharge limits which may include setting maximum discharge limits based on soil contaminant levels"

To "consider", the regional authorities of NZ require identification and knowledge of the major issues, the consequences to the environment and to human wellbeing of human activities, to identify where issues may arise in the future, and ascertain what issues are of greatest immediacy. Also needed are tools to assess the effectiveness of their policies in managing these issues. This thesis increases knowledge of the fate of trace elements applied to land in fertilisers that may underpin the "consider" process and provide a baseline for

assessing policy effectiveness. Specifically, regional authorities of NZ can assess the effectiveness of their policies in managing diffuse contamination of trace elements associated with fertiliser application.

1.3 Perturbation of biogeochemical cycles

Perturbation of biogeochemical cycles has resulted in the need for regulation by authorities. The fate of trace elements from phosphate fertiliser has been identified as a global question. At the global scale, soil is the central component of the critical zone of life. Soil does not exist in isolation, but interacts with the physical world. The physical world has been traditionally classed into four major subdivisions or environmental compartments (Kim & Taylor 2009):

- atmosphere (5.14 x 10^{15} tonnes of air),
- hydrosphere (1.5 x 10^{18} tonnes of freshwater, ice, ocean water and dissolved salts),
- lithosphere (2.4 x 10^{19} tonnes of the Earth's crust to 17 km),
- biosphere (8 x 10^{12} tonnes of living things, mainly organic material). The biosphere is a thin film on the Earth's surface.

Cycling of metals between these four environmental compartments (biogeochemical cycling) occurs as a result of interchanges of matter and energy. Important transport routes between the three inanimate compartments are summarised in Figure 1.5.

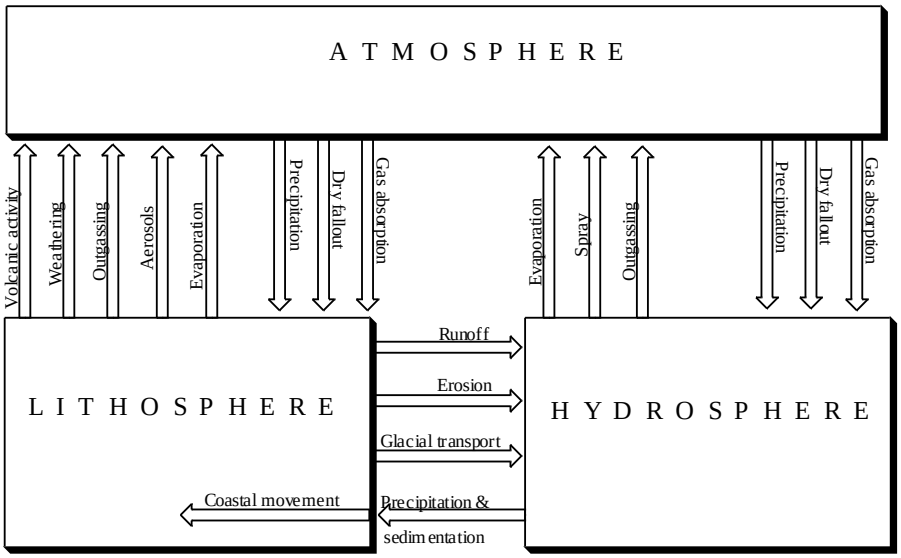

Figure 1.5: Processes involved in cycling of trace elements between the atmosphere, lithosphere and hydrosphere (Kim & Taylor 2009).

Before the global industrial age, metal fluxes between the environmental compartments due to natural biogeochemical cycling were (more or less) at steady-state. Since then, the widespread anthropogenic use or dispersal of trace elements has meant that fluxes from anthropogenic sources, including application of trace elements in fertiliser, are now substantially larger than the approximately steady-state fluxes associated with natural sources. The result has been a perturbation in biogeochemical cycles where input rates into some compartments have overwhelmed the available output paths, leading to a gradual accumulation of metals in those compartments. One of the results of this perturbation is a net accumulation of some trace elements in soils, terrestrial environments, the food chain and the biosphere (Kim & Taylor 2009).

On average, agricultural soils tend to accumulate trace elements at a much faster rate than uncultivated or natural state soils due to direct additions, e.g. trace elements in fertilisers. Soils can also become depleted or deficient in some trace elements as a result of the increased losses associated with particular land use practices. The significance of these changes is often unknown, but in some cases soil resource capacity could be lost through the accumulation or deficiency of one or more trace elements, e.g. through adverse effects on stock health or productive capacity, decreased microbial function, onset of phytotoxicity, non-compliance with food standards, and non-compliance with soil guidelines designed to protect human health.

Other impacts caused as a result of the soil acting as both a sink and reservoir for trace elements may include the potential for their movement across environmental compartment boundaries as concentrations in soil increase and adsorption capacity is overwhelmed. Cross-compartment movement may have a beneficial fertilisation effect or negative impacts, such as toxicity to aquatic invertebrates and accumulation of trace elements in offsite receiving environments, e.g. freshwater lake sediments or coastal areas. Although it seems likely that a proportion of the trace elements applied in fertiliser are finding their way to associated stream, river and lake sediments, little is known about the rate and significance of cross environmental compartment movement/accumulation at present (Kim 2005). This thesis seeks

to improve understanding of which trace elements are most likely to move across environmental compartments and their magnitude. Due to limits of space and time, this thesis limits its subject to a systematic evaluation of the range and quantity of trace elements applied to land in organic and mineral P fertilisers and their wider environmental impacts.

1.4 Characteristics of NZ soils and sediments

The characteristics of soils and sediments affect the behaviour of applied trace elements of fertilisers, especially their mobility, thus their ability to transfer to water or availability to plant uptake. The same pedological processes (Mortimer 1950, Ponnamperuma 1972), microbial activity (Murphy et al. 1972) and organic enrichment (Holmer et al. 2005) take place in sediments and soils but there are some important differences. Soils require time and a stable ground surface to develop a soil profile, while sediments are a collection of particles redeposited elsewhere by water, wind, or glaciers. Soils are exposed to the earth's atmosphere and undergo periods of wetting (due to rain and floods) and drying, while fluvial & lacustrine sediments generally stay wet. In general, sediments sink and accumulate on the bottom of lakes, rivers estuaries and the ocean bed in areas of slow moving water (USEPA 1998).

In soil, many trace elements applied in fertiliser are strongly adsorbed onto surfaces of mineral and organic phases, while others remain mobile and readily transfer to ground or surface waters, or are taken up by plants. However, these soil particles can themselves be transported to waterways by erosion processes or as colloidal particles (Kretzschmar & Schäfer 2005). Fixation of trace elements by soils is a dynamic and partially reversible equilibrium process. Soils can act as ‘metal-ion buffers’ by fixing trace elements applied in fertilisers, but also act as reservoirs for trace element release at a later time.

In the sediment, the mineral matter may sorb some trace elements by adsorption, while the sediment organic matter may also sorb trace elements by partition processes, where some dissolved trace elements partition into the matrix of the entire sediment organic matter (Chiou & Kile 2000). Like soils, sediments can act as ‘metal-ion buffers’. Elements such as As, Cd,

Cr, Cu, Hg, Ni, Pb, and Zn have been shown to accumulate in sediments, resulting in risks to the aquatic environment (Vignati & Berlinsky 2010).

The soils of NZ are, generally, deficient in most nutrients including N, P, S, B, Co and Se, i.e. the soils do not contain enough of these elements in plant available form to meet plant growth requirements in horticultural or pastoral agricultural systems (Figure 1.6). Intensification of farming practices exacerbates deficiencies, which must be overcome by greater additions in fertiliser. Some essential elements are present in very low concentration in particular soils, while others are present in considerable amounts in the soil but are bound so tightly to the soil matrix as to be effectively unavailable; e.g. the average total I concentration in NZ soils (7.4 mg/kg) is at the high end of world averages (4-8 mg/kg) and above levels typically associated with I deficiency (McNally 2011). However, I is tightly bound to soil so little is taken up by plants. As a result, the population of NZ is deficient and I is supplemented in table salt.

Figure 1.6: A New Zealand landscape. The greener fields demonstrate the effect of fertilisers (M D Taylor).

The sorption capacity of NZ soils is generally high for both cations and anions. This high sorption capacity is due to the naturally high C content of the soils (average native background sites 8.4%) and the presence of amorphous hydroxides (Appendix 1.2). In addition, soil pH is typically slightly acid and most soils are well oxidised. However, the wet, temperate climate of NZ leads to periods where the soil is water-saturated. The combination of these characteristics can result in the availability of pH-dependent sorption sites, sites for organo-metal complex formation and very high anion adsorption capacities (Fageria 2009). The periodic changes in redox potential from wetting and drying cycles can also result in precipitation of Fe and Mn with coprecipitation of trace elements (Figure 1.7). All these natural soil characteristics impact on the fate of trace elements applied in fertilisers.

Figure 1.7: Photo of Fe (brown) and Mn (black) concretions precipitated due to periodic wetting and drying cycles in a Te Kowhai silt loam from Waikato, New Zealand (Peter Singleton, Waikato Regional Council).

Sediments, on the other hand, generally remain water saturated, while the surface is better oxygenated than the deeper sediments (Zwolsman et al. 1993).

1.5 Agriculture and fertiliser use in New Zealand

The majority (86%) of the 4.5 million residents of NZ live in urban areas, while rural areas are extensively used for agriculture and horticulture practices. About 55% of land area in NZ is used for primary production, with 41% pastoral, 7% production forestry, 2% cropping and horticulture and 6% farm infrastructure, river beds and scrub (Statistics NZ 2011).

Fertiliser applications are essential for successful agricultural production in many nations, including NZ, as fertilisers supply essential nutrients for plant growth. The agricultural industry dominates the economy in NZ, with international trade indispensable to New Zealand's agricultural industry and economy, which depends in turn on factors such as consumer demand, international regulation, and the wider economic and geopolitical situation for the wellbeing of the population. Also, agricultural production is underpinned to a large extent by phosphate fertiliser, a major source of Cd (Taylor et al. 2007) and possibly other trace elements into agricultural soils (McLaughlin et al. 1996).

In NZ, continual applications are necessary to replace nutrients removed in produce or lost from the soil root zone. Because much of NZ is undulating and difficult to apply fertiliser to by conventional surface applicators, topdressing using aircraft was developed during and immediately after the Second World War (Figure 1.8). Many high country farms in NZ have their own airstrip for topdressing aircraft to load fertiliser and lime. Fertiliser moves sideways in both directions as a result of the air turbulence when dropped by aircraft (Figure 1.9). The application rate is much greater in the centre of the flight path than the sides, so the pilot overlaps successive flights to even out the overall application (Maber 2012). In NZ, fertiliser applications have allowed increases in production and farming on land not previously suitable because of low fertility.

The environmental problems with excess nutrients causing eutrophication of surface waters and the accumulation of Cd are well documented (Jarvie et al. 2015, Singleton 2008, Taylor et al. 2006). However, fertiliser application can have positive environmental consequences, e.g. the enhancement of plant cover and decreased area of bare land. The reduction of bare land

leads to lower levels of erosion and to a reduction in nutrient and contaminant migration to surface water. Also, soil carbon levels can increase as a result of enhanced biological activity (Fageria 2009).

Figure 1.8: Early topdressing aircraft used to apply fertiliser in NZ (John Maber. 'Topdressing - Fertilisers and spreading methods', Te Ara - the Encyclopaedia of New Zealand).

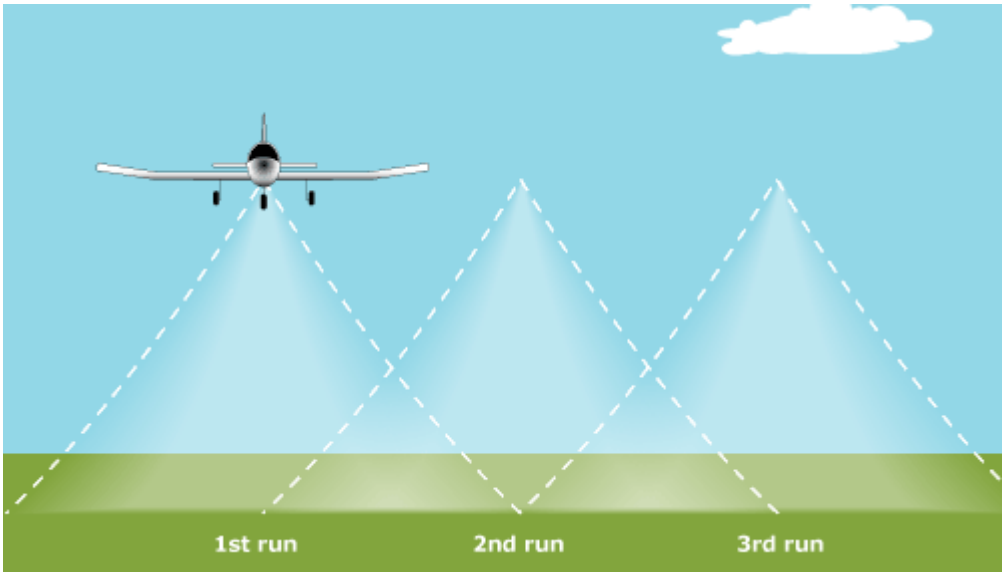

Figure 1.9: The fertiliser spread pattern: The application rate is much greater in the centre of the flight path than the sides, so the pilot overlaps successive flights to even out the overall application (John Maber. 'Topdressing – Spreading fertiliser, Te Ara - the Encyclopaedia of New Zealand).

1.6 Historical use of fertiliser in NZ

Deficiencies in major nutrients and trace elements are common in NZ soils, in particular the two main elements P and N (Cornforth, 1998). The development of commercial farming during the 19th century led to a realisation that inputs of fertiliser were needed to supplement these deficient soil nutrients. Single superphosphate (SP) was found to be most suitable fertiliser at this time and amounts of about 150 -250 kg per hectare were initially applied (CWG 2008).

Use of phosphate fertiliser increased steadily and dramatic increases in production were obtained. Between 1961/62, when reliable records were first kept, and 1979/80, the use of phosphate fertiliser in NZ doubled from one to two million tonnes per annum (96,200 t P to 180,100 t P, CWG 2008).

The removal of subsidies on fertiliser in the 1980s had a dramatic impact on fertiliser use, which decreased from an estimated 1,996,000 tonnes in 1979/80 to a low of 836,500 tonnes in 1988/89 – the lowest level in more than a quarter of a century. Following this downturn, there was a steady increase in the amount of phosphate fertiliser used, to a high of 2,230,000 tonnes of phosphate fertilisers in 2002/03 (or 220,900 t P, CWG 2008).

1.7 Current phosphate fertiliser use in NZ

By mass, SP use is the dominant fertiliser in NZ, about 87% of phosphate fertilisers applied (CWG 2008). Within pastoral agriculture, dairy farms use the most phosphate fertiliser. Application rates are typically 200-600 kg ha^{-1} y^{-1} with intensive dairy farming applying superphosphate at the upper end of this range, whereas the more extensive farming operations (sheep, beef and deer) tend to apply the smaller amounts (Mills et al. 2004). In a 1992 survey, 22% of pastoral farms were applying more than 600 kg ha^{-1} y^{-1} (CWG 2008).

Horticulture, requirements vary from crop to crop, with potatoes requiring the highest loadings of phosphate, typically 800 -1000 kg ha^{-1} y^{-1} SP or DAP. Mills et al. (2004) reported after discussions with growers that asparagus and apples receive SP at application rates of 200 - 400 kg ha^{-1} y^{-1} and 100 - 200 kg ha^{-1} y^{-1}, respectively.

Currently, Morocco is the dominant source of phosphate rock used for SP manufacture in New Zealand (CWG 2008). Decisions by countries with low cadmium rock to classify phosphate rock as a 'strategic material' has resulted in these sources of supply becoming unavailable to New Zealand, e.g. in 2004, the Government of China imposed limits on exports of phosphate rock, and so it is currently unavailable to New Zealand (USGS 2004).

1.8 Trace elements in fertilisers

Both mineral and organic fertilisers are known to contain trace elements as impurities (McLaughlan et al. 1996). These trace elements in fertilisers are either derived from the raw materials from which fertilisers are manufactured or are introduced during the manufacturing process, e.g. H_2SO_4 used to acidify the raw phosphate rock may contain Hg as a contaminant (Mirlean et al. 2008). However, introduction during manufacture is uncommon and the dominant sources of fertiliser trace elements are the raw materials used to manufacture P and micronutrient fertilisers (Stacey et al. 2010).

Pure N and K fertilisers generally contain much lower concentrations of trace elements than other types of fertiliser (McLaughlan et al. 1996). In comparison, mineral P fertilisers are considered as one of the most important diffuse sources of trace elements in agricultural soils. McLaughlan et al. (1996) reported the most common trace element metals, metalloids and radionuclides found in P rock were As, Cd, Cr, F, Hg, Pb, Se, U and V. In NZ, major industries, such as dairy companies, do not allow their supplier farmers to apply fertiliser derived from sewage products, so fertilisers from this source were also excluded. Thus, this study focuses only on mineral P fertilisers and fertilisers derived from organic material other than sewage products.

There are two types of P rock deposits, sedimentary and igneous. Sedimentary deposits often contain higher concentrations of trace element impurities compared to igneous deposits (Stacey et al. 2010). Sedimentary deposits are generally associated with matter derived from living creatures and thus contain organic compounds. These phosphates are interposed with sedimentary and gangue minerals and thus sedimentary P rocks have differing compositions

within the same source. As a result, trace element concentrations of raw P rock vary widely between deposits within countries, e.g. Cd concentrations varied between 3 and 150 mg kg^{-1} in samples from Florida and Idaho, USA, respectively (van Kauwenbergh 1997, quoted in Stacey et al. 2010).

In addition, most phosphate ores have to be concentrated or beneficiated before they can be used. Different techniques may be used at the beneficiation stage, to treat the same ore for removal of the gangue and associated impurities, e.g. SP is manufactured by reacting H_2SO_4 with P rock, with all of the metal trace elements present in P rock transferred to the final SP product. In contrast, triple superphosphate (TP) is manufactured by reacting H_3PO_4 with P rock and produces a phosphogypsum byproduct. The impurities in the original phosphate rock are proportioned between the product P fertiliser and the phosphogypsum, e.g. U mainly goes into the phosphoric acid but any Ra, which is a component of the U decay series, is co-precipitated with the phosphogypsum (EFMA 2000). This gives rise to further variations in the trace element composition of the finished fertiliser product.

Organic fertilisers can also contain appreciable amounts of trace elements, but also be an alternative source of P. The trace element contribution reflects the diet of the animals or plants that contributes the raw materials for the organic fertilisers. While the trace element contributions of organic fertilisers may be unexpected by some, the effects of agricultural intensification, including feeding of growth enhancers, has been known for some time, e.g. Eck & Stewart (1995) stated, "Depending on the degree of intensification of livestock feeding, animal manures have turned from a precious resource into a waste product". A key message is to choose the raw material of fertiliser, whether mineral or organic, wisely.

Two alternative strategies have been proposed to reduce contaminant trace element concentrations in mineral phosphate fertilisers. They are to preferentially mine low-contaminant phosphate rock or to blend high- and low-quality rock to reduce contaminant levels to more acceptable levels (Stacey et al. 2010). However, decisions by countries with low cadmium rock to classify phosphate rock as a 'strategic material' has resulted in these sources of supply becoming unavailable to New Zealand (Section 1.7). Similarly, reduction of

contaminant trace elements in organic fertilisers depends on identifying a “clean” source of raw material.

1.9 Previous studies on the environmental effects of long-term application of trace element contaminants of P-fertilisers

Due to the concerns stated in section 1.8 above, there have been numerous studies carried out by researchers investigating the environmental effects of long-term application of fertilisers derived from P rock.

Unease about the increasing use of F-containing phosphate fertilisers and inorganic pesticides lead to detailed research on soil F in the 1930s and 1940s. This resulted in advances in understanding the mineralogy of soil F, concentrations in different soil types worldwide, and the chemical species present (Davison & Weinstein 2006). There was usually a measurable increase in the F content with depth due to leaching in humid climates, as long as the soil was unploughed and there was no significant deposition of F from fertilisers, volcanic ash or industrial sources. However, where F-containing fertiliser was applied, higher concentrations of F could be seen in the topsoil (Robinson & Edgington 1946, Gemmell 1946, Omueti & Jones 1977, Loganathan et al. 2001). While studies addressed the distribution of F in agricultural and non-agricultural soils, little work investigated the effect of P fertiliser application on F accumulation or mobility (Loganathan et al. 2001). Interest in F declined until McLaughlin et al. (2001) warned chronic fluorosis in stock may develop in the next two to five decades due to accumulation in soil. A response was a body of research investigating the effects of the application of F on farm animal health (Loganathan et al. 2008, 2007, 2006, 2001, Hedley et al. 2007).

Following on from the work of the 1930s and 1940s, Schroeder & Balassa (1963) drew attention to Cd accumulating in soils and crops due to applications of phosphate fertilisers. Several studies were initiated with most endeavour focussed on Cd, e.g. Rothbaum et al. (1986) showed that years of phosphate rock and superphosphate application increased soil Cd levels in pasture soils. However, Cd did not significantly increase in soil under arable crops.

In NZ, great quantities of phosphate fertiliser are required for intensive pastoral farming, resulting in Cd accumulating in soil (Roberts et al. 1994). As NZ has traditionally sourced its phosphate from high Cd P rock, i.e. the ancient avian guano deposits of Christmas Island (42 mg Cd kg^{-1}) and Narau (100 mg Cd kg^{-1}) (Syers et al. 1986, Truman 1965), considerable accumulation of Cd was observed (McIntosh et al 1997, Taylor 1997a). Another unfortunate management practice was to store fertiliser directly on the ground during aerial topdressing operations (Figure 1.7). This resulted in localised areas of contamination (Taylor 2006, Taylor & Percival 2001).

Cd is sorped by soil organic matter (Taylor & Theng 1995, Parfit et al. 1995) and accumulation was greater in the organic fraction of soils (Rothbaum el al. 1986). However, about 20% of the applied Cd was not accounted for (Rothbaum el al. 1986) and elevated soil solution Cd was associated with higher P fertiliser additions (Taylor & Percival 2001, Taylor et al. 2008). Addressing Cd in the marine environment, Augar et al. (2015) showed advection processes limit the residence time of water masses resulting in a low natural Cd-uptake by plankton communities while anthropogenic Cd-uptake is high.

There is a smaller body of research on the fate of U impurities of P fertilisers. As mineral soils form from the weathering of rocks, U concentrations in soil are in the same order as for rocks, ranging from 0.79 to 11 mg kg^{-1} with an average of between 1 and 2.5mg kg^{-1} (Kabata-Pendias & Pendias 2001, Edwards et al. 1995, Schnug et al. 1996), consistent with soil parent material being the major source of U. Soil U concentrations may be increased by deposition of particulate matter, fly ash, decomposition of plants and animals, and application of sewage sludge and fertilisers (Edwards et al. 1995).

The quality of surface and ground waters may be reduced by U in agricultural runoff (Zuur 1995, Zielinski et al.1995). Fertiliser derived U may also enter drinking water supplies through leaching into ground and surface waters (Hassoun and Schnug 2011, Smidt et al. 2011). Elevated U concentrations in waters associated with the application of phosphate fertilisers to agricultural soils have been reported in Belgium, Brazil, Croatia, Germany, Italy, Mexico, Eastern Slovenia, Spain and Syria (Cuoco et al. 2015, Fiket et al. 2015, Vandenhove

et al. 2015, Hoyer 2015, Hassoun and Schnug 2011, Smidt et al. 2011, Barišić et al. 1992, Spalding & Sackett 1972). Jones (1992) and later Hamamo et al. (1995), studying U in the Morrow Plot soils over 85 years, found U increased (possibly from lime or phosphate fertiliser) then declined rapidly, implying removal in crops or leaching to groundwater. On the other hand, U applied in P fertiliser was shown to accumulate in Australia, Ireland, German, NZ, Japanese and UK soils (Lottermoser 2009, Tunney at al. 2009, Utermann & Fuchs 2008, Taylor 2007, 1997b, Takeda 2006, Rothbaum et al. 1979).

Rothbaum et al. (1979) found U to have accumulated an average of 0.45mg kg^{-1} in topsoils from Rothamsted Experimental Station fertilised with about 33 kg P/ha/y as superphosphate since 1889. In NZ, the concentrations of U in fertilisers derived from the ancient guano deposits mined from Nauru and Christmas Island (Trueman 1965) ranged from 31 - 56 mg U kg^{-1} for Christmas Island and from 64 - 121 mg U kg^{-1} for Nauru Island (Williams 1974, Syers et al. 1986). The accumulation rate for total U in NZ soils ranged from 15-47µg kg^{-1} y^{-1} following the fertiliser application rate in a study of 4 sites (Taylor 2007) and all the added U could be extracted in nitric acid (Taylor & Kim 2008, Taylor 1998, 1996).

Accumulation of some other mineral fertiliser associated elements in soils has also been identified but not studied in detail. Sauerbeck (1993) carried out a hazard ranking of potential contaminants in P fertilisers by examining the range of trace element concentrations in phosphate rocks and comparing this to average elemental concentrations in the earth's crust. As well as Cd, F and U, this ranking study identified that As, Cr, Sr, Th, and Zn should be further investigated. In another study, McLaughlan et al. (1996) reported the most common trace element metals, metalloids and radionuclides found in P rock were As, Cr, Hg, Pb, Se, and V. A third assessment by the USEPA reported potential human health risks of concern were from only As and dioxin congeners found in select liming agents and micronutrient fertilisers but none were reported for P fertilisers (USEPA 1999). However, a systematic assessment of the fate of these mineral fertiliser associated elements in the wider environment does not appear to have been carried out and the literature shows disagreement on what is important.

There have also been several studies on the contributions of trace elements from organic fertilisers and manures (Bolan et al. 2010, 2004, Luo et al. 2009, Uprety et al. 2009, McBride & Spiers 2001, Mortvedt 1995). Manures were found to contribute significant amounts of Cd, Cu and Zn, while poultry litter contributed As, Cu, Mn, Ni and Zn. The fate of trace elements in a range of biosolids from Christchurch City, NZ and fertiliser products was examined in a 3 year study using barrel lysimeters. Cd, Cr, Cu, Ni, Pb and Zn accumulated in the topsoils, while Cd, Ni, and Zn in drainage were also elevated. (McLaren et al. 2003, 2004, 1999a, 1999b). In addition, nematode populations were affected by the high concentrations of metals (Yeates et al. 2006).

There have been no large-scale assessments to determine the fate of inputs of fertiliser associated contaminants to agricultural soils that have now received about 65 years of intensive annual P-fertilisation.

1.10 Previous priority assessment models

Models and risk assessments seeking to describe the movement and the fate of diffuse contaminants have addressed greenhouse gases (Scholeze et al. 2006), major nutrients N and P (Heathwaite et al. 2005, Skinner et al. 1996, Sharpley et al. 1994) and microbial contaminants (Tian et al. 2002).

However, there does not seem to have been a systematic assessment published of the range and quantity of trace elements applied to land as in fertilisers, nor their movement and fate as they cross environmental compartments. This is despite interest, especially in agricultural areas, about the wide-spread application of trace elements in fertilisers (McBride & Speirs 2001). In one approach, impacts on the marine environment from land-based sources were investigated using a Lagrangian approach to compare the potential transfer of Cd from natural and anthropogenic sources to plankton communities in the North-West African upwelling (Windom 1992, Augar et al. 2015). In addition, Molloy et al. (2005) scoped establishing a list of prohibited substances and guideline limits for levels of contaminants in fertilisers in Australia using a risk assessment approach.

Previous studies that cross environmental compartments have focused on threats to human and higher animal health (Oomen et al. 2003, Johnson & Ettinger 1991, USEPA 1999) rather than assessing consequences to the wider environment. Alternatively, studies have focused on the ecotoxicology or the fate of trace elements in a specific environmental compartment (Chapman et al. 2011, Robinson et al. 2007).

Sauerbeck (1993) carried out a hazard ranking of potential contaminants in P fertilisers by examining the range of trace element concentrations in phosphate rocks and comparing this to average elemental concentrations in the earth's crust, but this was a simple model and of limited practicable use by regulatory authorities. In comparison, within the management of contaminated sites research, a model was developed for describing transport and loss of soil-applied organic chemicals (Jury et al. 1983). This allowed the authors to classify and screen organic chemicals for their relative susceptibility to different loss pathways (volatilization, leaching, degradation) in the soil and air. Similarly, a national scale contaminant fate model for Canada was used to describe the fate of benzene, trichloroethene, and diethylhexyl phthalate (Woodfine et al. 2002). Ecological regions, which were previously treated individually, were linked with flows of air and water deduced from GIS analysis to provide a comprehensive description of long-range transport between regions over the entire country.

The USEPA carried out a risk assessment that estimated potential risks posed to human health by contaminants in fertilisers, including P fertilisers (USEPA 1999). However, the analysis did not include a comprehensive evaluation of ecological risks. It used a probabilistic methodology to estimate the incremental increase in lifetime cancer risk and/or noncancer health effects associated with exposure to hazardous constituents contained in fertilisers and other agricultural soil amendments. Receptors evaluated in this analysis were farmers and their children. The assessment evaluated the risks from 9 metals (Cd, Pb, As, Cr Hg, Ni, V, Cu, and Zn) and 17 dioxin congeners potentially contained in each of 13 fertiliser products. The recognised contaminants found in P fertilisers (F and U) were not addressed by this study. Also, the groundwater exposure pathway (i.e. the ingestion of contaminated groundwater) was not evaluated for this analysis of risk.

USEPA (1999) reported that only a few of the large number of fertiliser products evaluated had contaminant levels high enough to potentially cause cancer risk or noncancer hazards of concern. This assessment showed that potential human health risks of concern were from only As and dioxin congeners found in select liming agents and micronutrient fertilisers.

Another consideration in assessing the likelihood of ecological impact of trace elements in P fertiliser applications is identifying a change in concentration above spatial variability. Spatial variability may be due to inconsistent inputs, uneven application, and the removal in produce or losses in leaching, erosion and overland flow depending on the properties of the element concerned, site climate and the soil properties. Taylor (2007a) reported considerable variability within two paddocks at different farms that had been used to store SP fertiliser before it was spread over the farmland (Figure 1.10). However, representative samples for each site were obtained by compositing 30 soil cores (25 mm wide by 150mm depth). So, mass loadings need to be considerable to detect accumulation of trace elements in fertilised soils; accumulative fertiliser applications must be large, along with high concentrations of trace elements being present in the fertiliser (Stacey et al. 2010).

Long-term trials, such as those at Rothamsted, or continuous monitoring programmes, such as Soil Quality Monitoring in NZ (Kim & Taylor 2009), are invaluable for assessing the fate of trace elements in fertilisers as they allow enough time for cumulative applications of fertiliser to reach a critical mass loading. If an element added to the soil is not accumulating, then it must be removed in produce or lost in leaching, erosion and overland flow. Removal of trace elements from fertilised soils may be large for elements that do not bind strongly to the soil matrix (i.e. have a low partition coefficient), so are prone to leaching or to partition into soil solution and be more readily available for plant uptake, e.g. B.

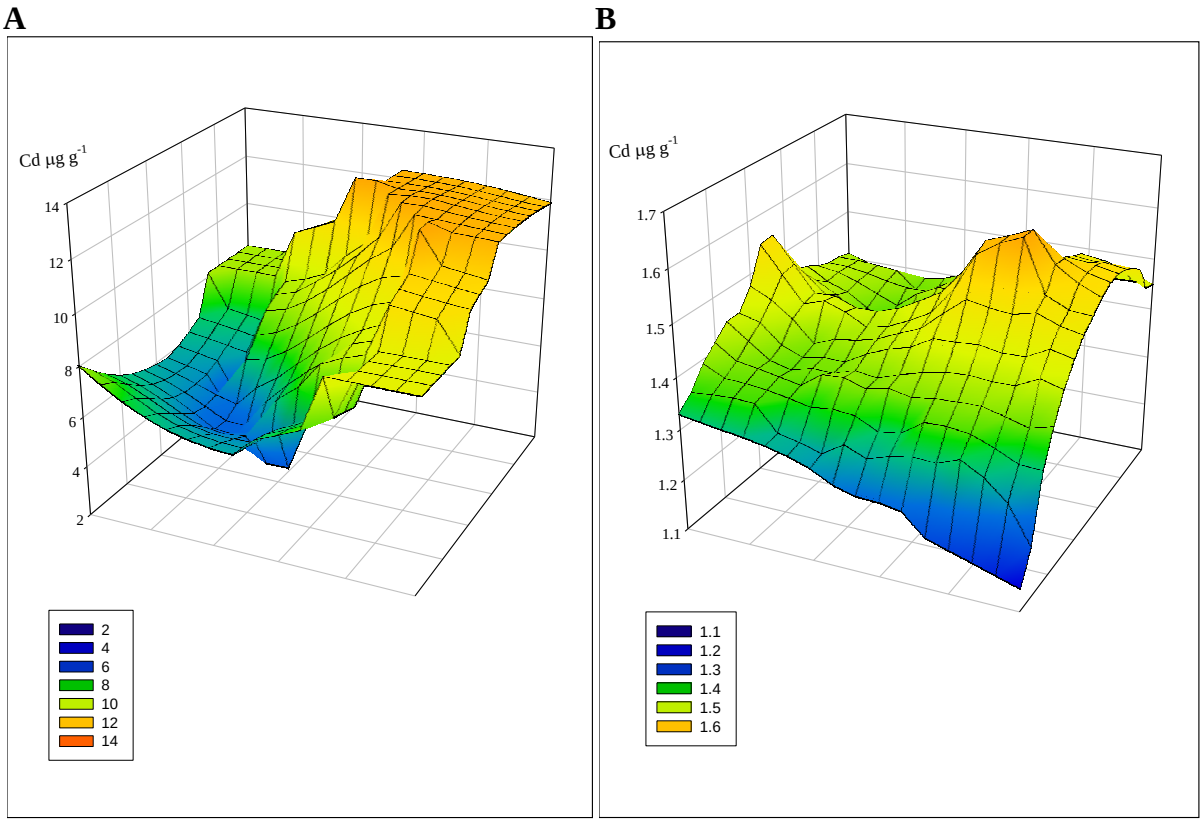

Figure 1.10A: Cadmium concentrations in an Organic soil from a paddock previously used to store phosphate fertiliser (Taylor 2007).
Figure 1.10B**:** Cadmium concentrations in an Allophanic soil from a paddock previously used to store phosphate fertiliser (Taylor 2007).

1.11 Setting a baseline

Studies on environmental contamination often suffer from the lack of reliable information on the natural background of trace elements to act as a baseline (Pfeifer et al. 2000). The natural background concentration of trace elements is the concentration that would exist in the absence of human input. The composition of the lithosphere, i.e. the dominating rock type, strongly influences the natural trace element contents and fluxes of local ecosystems.

Background concentrations of elements are important considerations for risk assessment for two reasons. Firstly, organisms adapt to the background concentrations of elements in which they have evolved, so that toxicity thresholds for organisms in high background environments are greater than those adapted to low background environments (McLaughlin and Smolders, 2001). Secondly, some trace elements exist naturally over a wide range of concentrations and

a toxicity limit may easily fall within the background range. Thus, insufficient knowledge of this natural contribution can lead to misinterpreting contamination.

Another consideration is, in the absence of man, the dispersion of trace elements in the different environmental compartments is mainly governed by weathering and mass transport (Pfeifer et al. 2000). However, the natural background pH of the soil and water compartments also strongly influences sorption behaviour and thus retention or release of specific elements. Soils formed on silicate rocks usually exhibit acid conditions (pH 4–6.5), soils related to groundwaters are typically near neutral (pH 6.5–7.5), while soils and waters related to carbonate rock environments are usually neutral to alkaline (pH 7–8.5, Pfeifer et al. 2000). NZ soils are nearly all naturally acidic (Section 1.4, Appendix 1.2).

The addition of trace elements adds to the existing background content and may overwhelm the natural equilibrium. However, impacts on ecosystems are usually minor if the contaminant levels applied are not significantly above background (2.5 times, Kim & Taylor 2009, Kim et al. 2008).

Thus, background measurements of trace elements in soils are a useful baseline to assess changes caused by the addition of trace elements from anthropogenic activities, including fertiliser addition. Background concentrations can be estimated by using one of three methods (Kim & Taylor 2009):

1. Soil sampling at native reserve sites where no direct human use has occurred. This is the most common method. Uncertainty about the history of a site can make it difficult to determine whether it does represent a "true" background location. However, this approach is more applicable in countries where historic and current atmospheric inputs of trace elements to soils from industrial sources are negligible. Therefore, background sites are usually well removed from urban areas.
2. Retrospective analysis of archived soil samples.
3. Determination of the intercept of an element-element scatter plot to estimate background concentrations in productive soils, without recourse to actual background sites (Figure 1.11). However, this only applies in cases where a good correlative

relationship exists between two anthropogenically-derived elements, and it has been shown that one source is responsible for all of the observed enrichment, e.g. for P-F, mass balance can be used to show that nearly all the additional P and F can be accounted for by use of P fertilisers.

Similarly, measurements of pristine, high value water, such as Lake Taupo or the headwaters of the Waikato River in NZ, can provide a baseline to categorise fertiliser trace element impacts further downstream.

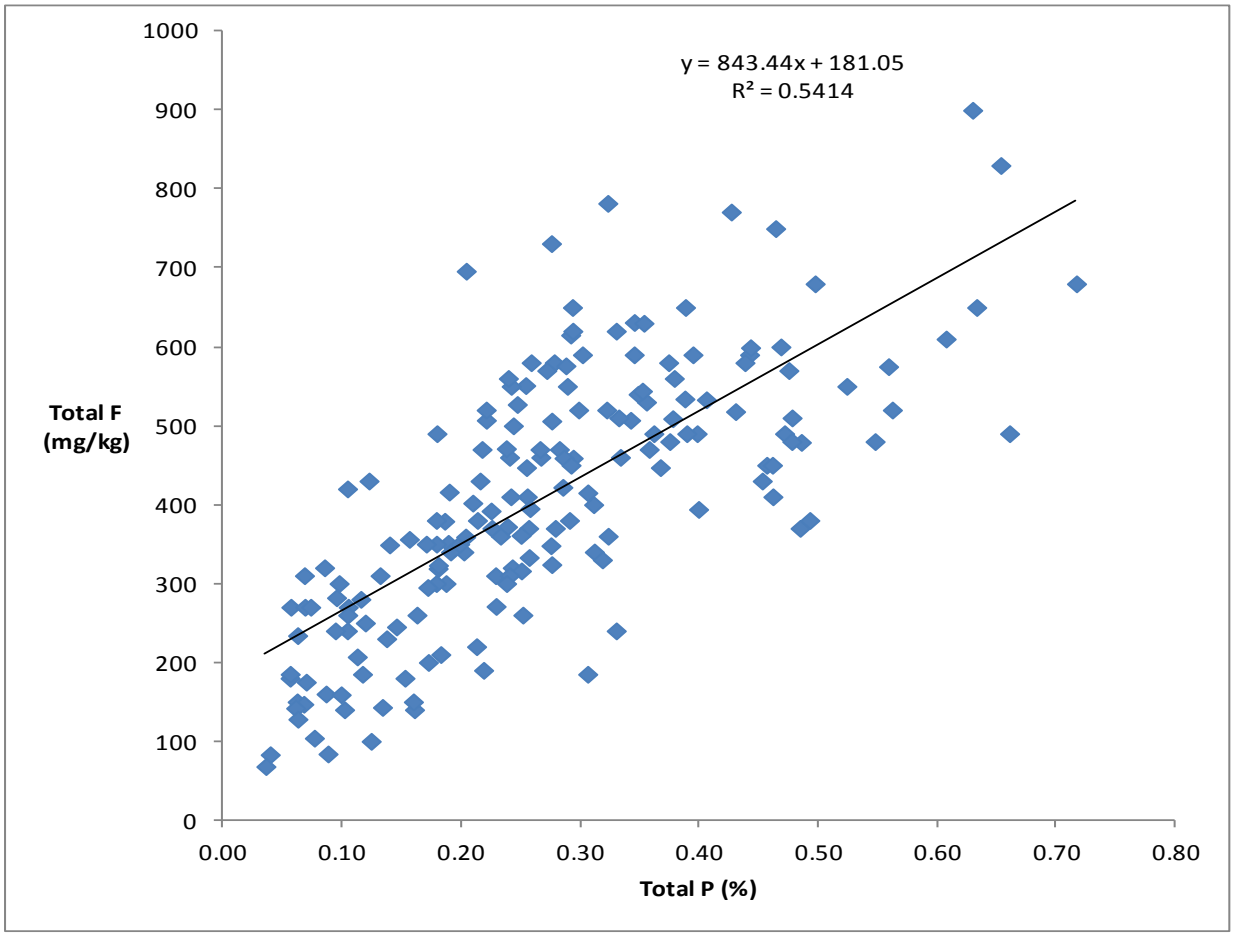

Figure 1.11: Determination of the intercept of a P-F scatter plot to estimate background concentrations of F in productive soils. The average natural background level for P is 0.03%, which provides an estimate (205 mg kg^{-1}) of the background concentration of F (Data from Appendix 1.2).

1.12 The fate of trace element contaminants of fertilisers

There is general interest in the fate of trace elements applied to soil in fertilisers as these can accumulate in soil, be taken up into the food chain or be transported to water or volatilise into the air. They can have either positive or negative effects on soil organisms, plants and higher animals (de Vries et al. 2007a). Plant uptake raises the potential for higher trace element concentrations in some food products. Although higher concentrations of deficient trace elements is clearly beneficial, excessive levels of trace elements in food can have implications for human health, market access, trade, and the ability to change from one land use to another (CWG 2008).

Several factors affect the fate of trace elements in soil and their transfer to other environmental compartments, i.e. partitioning between soil gaseous-, aqueous- and solid-phases. The distribution of trace elements between aqueous and solid phases of soils is described by the partitioning coefficient (K_d). Some trace elements are extremely insoluble with very high K_d values, e.g. Pb and Zr

However, partition coefficients are not constants, as they vary across soils due to variation in the amount and type of clay and organic matter, and due to the effect of soil pH on soil surface charge, and charge of the trace element, and the effect of redox on soil surface properties and on oxidation state of elements with redox dependent behaviour, e.g. As and Se. Another considerations is that soils with high K_d values have a high sorption or buffering capacity for added trace elements, i.e. the ability of the soil solid-phase to maintain constant concentrations of elements in the soil solution through sorption reactions. The buffering capacity is an integrated measure of the total amount of element, as well as the number and the strength of binding sites for that element in the soil. The buffering capacity of a soil is derived from the charged components, which include Fe, Mn and Al oxides, carbonates, clays and organic carbon. In soils with a high buffering capacity, the phytoavailability of trace elements is limited (Molloy et al. 2005).

Temperature affects their persistence in soils; directly by controlling transfer to the atmosphere (Henry's Law constant), e.g. Hg; and by its effect on contaminant solubility (K_d).

Indirectly, temperature controls microbial activity in soils which affects rates of degradation of organic matter levels, which determines contaminant partitioning (Molloy et al. 2005).

Rainfall leads to downward and lateral movement of elements to ground and surface water ecosystems. Rainfall also indirectly affects mobility, through its effect on soil organic matter levels (Molloy et al. 2005).

Fertiliser-derived trace elements occur in cocktails of multiple trace elements and sometimes organic contaminants are also present (McLaughlan et al. 1996). Trace elements show both competitive and cooperative interrelationships with each other but these are not yet fully understood (Ruters 2008). This adds to the uncertainty of the fate of these trace elements in the environment.

Once trace elements are mobilised they can have impacts on life at considerable distances from their origin. Sometimes the mobilisation process takes years or decades before the full impact is seen (Kim & Taylor 2009). Hence it is important to employ the precautionary principle when managing the impact of trace elements in the environment, including those applied in fertiliser.

Both essential and non-essential elements can become toxic at higher concentrations (Figure 1.12A & B). Some organisms have mechanisms blocking uptake of non-essential trace elements, giving them a competitive advantage and are only found on contaminated sites where they can express this advantage. These organisms have been used as indicators of trace element accumulation (Baker 1981). So either deficiency or excess of trace elements in soils can have a major bearing on soil health despite their low concentrations.

Although some fertiliser-derived trace elements may be taken up by biota for a period, they are likely released back to the soil by death and decay. Trace elements can shift association with different soil pools, becoming more or less mobile, while soil pH or redox conditions often have a major impact on trace element mobility. Also, interactions with other trace elements may make them more or less mobile (Kim & Taylor 2009). Under the same soil

conditions, some metals are more mobile in the soil than others and may be depleted in the root zone by plant uptake or leaching through the soil to ground and surface waters. Alternatively, root uptake of trace nutrients in plants and return to the soil surface by decaying plant material ("plant or vascular pumping") may serve to concentrate some elements in the surface soil relative to deeper layers (Steinnes and Njastad 1995). Those elements in a relatively immobile form, strongly attached to soil particles, can be transported to surface waters by erosion when water washes across the soil surface rather than infiltrating into the soil (Kim & Taylor 2009). Trace elements in fertiliser applied to land can also make their way to the sea and may change the sea's ability to sustain life and/or be aesthetically pleasing.

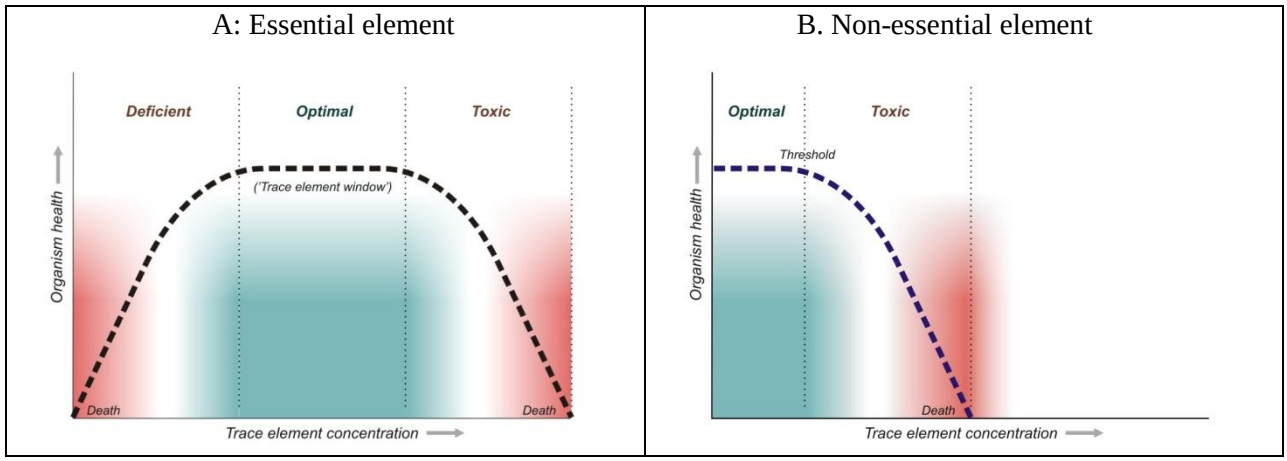

Figure 1.12: Relationship between health status and concentration for essential (A) and non-essential (B) elements (Kim & Taylor 2009).

The work presented in this thesis includes a systematic evaluation of the range and quantity of elemental contaminants applied to land in fertilisers and their wider environmental impacts. It addresses the retrospective assessment of a wide range of anthropogenic fertiliser associated contaminants in soils of NZ, across a representative range of natural and productive land uses, and soil orders, receiving real-world fertiliser inputs, and their transfer across environmental compartments. A systematic and transparent prioritisation methodology that is pragmatic and useful at the regional scale for regularity regional authorities, such as NZ Regional Councils is presented, including a model to assess the consequences to the environment and to human wellbeing from the application of trace elements, to identify where issues may arise in the future and what issues are of greatest precedence. Trace elements applied to soil in organic

fertilisers as well as those found in inorganic mineral P fertilisers were assessed. The modelled results are validated against the synthesis of a large national soil monitoring dataset and smaller ground and surface waters, and lake and estuarine sediment datasets. Such resulting rankings and the underpinning information can be used by policy makers, resource managers and researchers to guide decision making and allocation of priorities.

2 Material and Methods

2.1 Soil samples

2.1.1 Site descriptions and geocoding

Data from a total of 1242 soil samples from the Auckland, Bay of Plenty, Waikato, Hawkes Bay, Taranaki, Wellington Tasman and Marlborough regions of NZ were correlated (Figure 1.3). Sites were chosen and samples collected, stored and analysed following national guidelines (Appendix 2.1). Specifically, sites were chosen following Frampton (2009) and sampled following Hill & Sparling (2009) for soil quality monitoring parameters, while trace element parameters were sampled following Kim & Taylor (2009). The Waikato soil samples were collected by the author and other staff of the Waikato Regional Council. Soil samples from the other regions of NZ were collected by local regional council soil scientists along with professional soil scientist contractors (Gray 2014, 2013, 2012, 2011, HBRC 2014, 2013, 2011, Drewry 2013a, 2013b, 2012, Edmeades 2013, Guinto et al 2013, Guinto 2012, 2011, Campbell 2011, Burton 2009, MDC 2007, GWRC 2005).

Soils were classified according to the NZ Soil Classification (Hewitt 2010) and the World Reference Base for Soil Resources (Food and Agriculture Organization of the United Nations 1998). There were Allophanic soils (Andosols – 196 sites), Brown soils (Cambisols – 222 sites), Gley soils (Gleysols – 145 sites), Granular soils (Ferralsols – 94 sites), Melanic (Luvisols – 3 sites), Pallic soils (Lixisols – 116 sites), Podzols (Podzols – 21 sites), Pumice soils (Andosols – 136 sites), Recent soils (Fluvisols and Arenosols – 258 sites) and Ultic soils (Acrisols – 51 sites).

2.1.2 Sampling procedures

Samples were a composite of 50 cores, 2.5 cm diameter and 0-10 cm depth, taken from a transect of 50 m at each site.

Soil samples were collected from seven different land uses, namely long-term pasture for dairy cattle, (338 sites), other long-term pasture for sheep, beef cattle and deer (248 sites), cropping for vegetables (intensive 3 or more crops per year – 100 sites), production forestry

(radiate pine–133 sites), kiwifruit (30 sites), vineyards (43 sites), other horticulture for grains, citrus, persimmons, pip fruit and berries (135 sites) and native conifer–broadleaf bush (107 sites). There were 108 miscellaneous samples that did not fit into one of the above land use categories including urban sites, building sites, sports fields, schools and quarry sites. These miscellaneous sites were removed from the analysis. Trace element–land use interactions were presented at the NZ Soil Science Society Conference (Taylor et al. 2014a).

Samples from sites essentially unimpacted by man (distant from urban areas, roads and farm land, and unlikely to receive significant amounts of trace elements from aerial deposition) were considered natural background. Results from these natural background sites were presented at the NZ Soil Science Society Conference (Taylor et al. 2014b). The median values for each element were collated with 14 other studies of background concentrations in soils from 12 published sources to give the soil background values used in this study (Appendix 2.2). Combining this data this way provided a more robust estimation of soil background values.

2.1.3 Preparation and storage

Samples were prepared following Hill & Sparling (2009) for soil quality monitoring parameters, while trace element parameters were sampled following Kim & Taylor (2009). These procedures are presented in Appendix 2.1.

2.1.4 Meta data

A description of the soil profile was obtained following Hill and Sparling (2009, Appendix 2.1). Farmers were interviewed about their land management and this was recorded in an Excel spreadsheet.

2.2 Fertiliser samples

Data from 387 published sources and unpublished studies by Dr. Sylvia Kratz, Institut für Pflanzenbau und Bodenkunde, JKI and Dr. Geerd Smidt, EPI and the author's unpublished XRF data, collected during 1992-1999, were collated (Appendix 2.3). Data consisted of concentrations of total trace elements in 5161 inorganic N, P and K fertilisers, limes,

phosphate rock, and fertilisers derived from organic materials. Results from this assessment of fertiliser trace element data were presented at the NZ Soil Science Society Conference (Taylor et al. 2014c).

As explained in Section 1.8, P fertilisers are considered one of the most important diffuse sources of trace element contamination in agricultural soils, while pure N and K fertilisers generally contain low levels of trace elements (McLaughlan et al. 1996). This was born out by the data obtained as part of this thesis (Taylor et al. 2014c). In addition, the data showed organic fertilisers, such as composts, and derivatives of human and animal waste products, contained environmentally significant concentrations of trace elements. The trace elements may be present as an impurity or intentionally, as some fertilisers are deliberately fortified with various trace elements. Therefore, two groups, fertilisers derived from P rock and fertilisers derived from human, plant and animal waste products, which could be an alternate source of P, are the focus of this work (details in Section 2.2), giving a dataset of 5047 fertilisers.

Fertilisers were grouped according to type (Table 2.1). Data were not found for all elements for all types of fertiliser. Summary statistics are presented in Appendix 2.3 rather than in this section due to the size of the resulting table inhibiting the readability of the text. However, median values are presented in Table 2.2 to give a quick insight to the data. The concentrations of F in fertilisers derived from P rock are notable as they are well above concentrations normally associated with trace elements. For readability, F has been placed at the bottom of Table 2. World soil background values (Taylor et al. 2014b) have also been included in Table 2 for comparison.

Table 2.1: Descriptions of fertiliser groups

Fertiliser Group	Description
Ammonium phosphates (AP)	Salts of ammonium and phosphate
Superphosphate (SP)	Phosphate rock reacted with sulphuric acid
Triple superphosphate (TP)	Phosphate rock reacted with phosphoric acid
Blended fertilisers (BF)	Blended nitrogen phosphorous potassium fertilisers
Reactive rock phosphate (RRP)	Phosphate rock that is ground to very fine sand size and reacts with acids in the soil on application
Piggery	Derived from piggery manure and litter
Poultry	Derived from poultry manure and litter
Cattle	Derived from cattle manure and litter
Plants	Derived from plant material
Fish	Derived from fish

Table 2.2: Trace element median values for fertilisers and background soils (BG)

	Median (mg kg^{-1}): Fertilisers from P rock					Median (mg kg^{-1}): Fertilisers from organic materials					World BG soils median (mg kg^{-1})
Element	AP	SP	TSP	BF	RRP	Piggery	Poultry	Cattle	Plants	Fish	
Ag	0.18	1.74	0.30	0.07	0.20	0.01	-	0.05	0.12	0.30	0.09
As	7.41	7.63	11.0	2.91	7.68	0.91	3.3	0.60	5.20	1.00	4.8
B	133	178	452	221	495	19.5	34.0	21.4	2.50	0.50	24
Ba	20.0	45.7	88.7	105	549	58.2	43.0	47.1	118	0.15	354
Be	0.45	0.13	3.00	0.22	1.53	0.08	0.11	0.07	0.50	0.01	1.25
Bi	0.03	0.07	-	0.05	0.07	0.05	0.01	0.04	-	0.01	0.29
Cd	16.3	3.00	6.67	2.37	16.9	0.28	0.25	0.29	0.40	0.02	0.27
Ce	50.0	105	14.4	53.5	269	3.27	1.3	0.23	-	-	55.0
Co	1.55	2.54	1.36	0.98	1.36	1.39	1.5	0.60	3.90	0.22	8.0
Cr	102	29.7	83.0	24.8	114	6.27	8.5	3.45	13.4	0.12	42
Cs	0.93	0.37	0.22	0.40	0.40	0.21	0.09	0.12	-	4.20	4.6
Cu	22.5	27.0	18.0	11.9	17.0	197	75	17.8	23.7	6.80	16
Dy	6.48	10.97	4.10	7.48	-	-	-	-	-	-	4.0
Er	4.34	6.81	3.55	5.44	-	-	-	-	-	-	2.2
Eu	1.26	2.69	0.83	1.98	10.70	-	-	-	-	-	1.1
Ga	-	-	-	0.29	-	-	-	-	-	-	17
Gd	5.53	11.7	3.94	6.97	101	-	-	-	-	-	4.1
Ge	-	-	-	0.09	-	-	-	-	-	-	1.3
Hf	-	0.14	-	0.14	1.00	-	-	-	-	-	7.0
Hg	0.06	0.04	0.05	0.01	0.04	0.04	0.05	0.04	0.01	0.66	0.10
Ho	1.41	2.31	1.04	1.73	-	-	-	0.02	-	-	0.95
I	-	-	-	-	-	0.07	0.07	1.20	-	-	2.4
La	23.6	59.5	17.3	40.0	181	-	20.0	12.3	-	0.01	24
Li	2.95	1.20	2.65	1.20	5.50	-	-	2.70	-	0.33	25
Lu	0.70	0.96	1.00	0.59	2.30	-	-	-	-	-	0.38
Mo	3.52	2.96	5.51	2.63	5.67	3.6	3.57	1.95	1.00	0.66	1.5
Nb	1.39	0.84	0.30	1.65	-	-	11.0	-	-	-	12
Nd	24.2	53.8	13.2	36.9	140	-	-	-	-	-	25
Ni	24.4	24.9	25.2	11.0	22.4	7.1	12.0	4.44	4.85	0.10	15
Pb	1.53	6.66	5.00	2.60	5.95	2.3	7.33	2.85	5.40	0.10	21
Pr	2.41	13.17	2.51	8.61	-	-	-	-	-	-	8

AP = ammonium phosphates, SP = superphosphates, TSP = triple superphosphates, BF = blended nitrogen phosphorous potassium fertilisers, RRP = Ground phosphate rock, - = no data

Table 2.2 cont. : Trace element median values for fertilisers and background soils (BG)

	Median (mg kg^{-1}): Fertilisers from P rock					Median (mg kg^{-1}): Fertilisers from organic materials					World BG soils
Element	AP	SP	TSP	BF	RRP	Piggery	Poultry	Cattle	Plants	Fish	median(mg kg^{-1})
Rb	10.5	3.93	5.21	15.2	18.0	53.2	20.1	14.1	-	61.5	52
Sb	1.26	1.25	1.36	0.64	1.38	0.20	0.22	0.10	0.45	0.02	0.62
Sc	4.35	4.72	5.60	4.86	11.7	-	3.00	4.15	-	-	9.3
Se	1.35	2.27	2.68	1.06	2.54	1.1	1.12	0.58	-	2.50	0.38
Sm	4.93	18.3	2.87	2.44	40.5	-	-	1.26	-	-	4.4
Sn	0.29	0.45	0.52	0.20	0.29	0.07	0.07	0.09	-	0.01	1.2
Sr	73.0	1067	841	258	1423	61	61	42	-	0.12	100
Ta	-	-	-	0.08	0.70	-	-	-	-	-	1.2
Tb	1.00	2.61	0.87	1.15	6.60	-	-	-	-	-	0.57
Te	-	-	-	0.003	-	-	-	3.47	-	-	1.0
Th	5.52	1.48	3.92	2.86	3.90	-	-	-	-	-	9
Tl	0.31	0.36	0.32	0.16	0.45	0.06	0.06	0.04	-	0.03	0.36
Tm	0.65	0.88	0.54	0.65	18.1	-	-	-	-	-	0.40
U	53.8	33.5	94.9	29.9	79.0	2.1	1.82	0.17	-	0.0004	3
V	151	64.6	153	50.0	60.0	8.0	7.99	4.43	17.7	0.17	67
W	-	-	-	0.04	-	-	-	-	-	-	1.3
Y	64.7	98.3	66.0	81.6	123	1.2	1.18	0.58	-	-	21
Yb	4.93	5.45	5.00	4.00	7.90	-	-	0.05	-	-	3
Zn	136	126	280	110	181	512	362	101	163	179	60
Zr	16.2	16.5	21.1	21.2	788	-	-	-	-	-	259
F	19000	14600	21000	23000	31000	-	-	-	-	-	269

AP = ammonium phosphates, SP = superphosphates, TSP = triple superphosphates, BF = blended nitrogen phosphorous potassium fertilisers, RRP = Ground phosphate rock, - = no data

2.3 Surface water samples

Regional councils routinely carry out water quality monitoring to assess water health. Surface water samples were taken as part of regional council monitoring programmes by expert hydrologists following established standards, e.g. for the Waikato region, quality control measures are undertaken in accordance with Waikato Regional Council's ISO 9001:2008 standards including procedures for the collection, transport and storage of samples, and methods for data verification and quality assurance to ensure the consistency of data across the programme (Appendix 2.4). Samples are sent to IANZ registered laboratories for analysis. Back-up samples are held for two months until results have been verified by routine quality assurance procedures.

State of the Environment monitoring of surface waters for trace elements has rarely been carried out in New Zealand and data on trace elements were provided by three regions, Marlborough, Waikato and Wellington. For the Waikato region, water trace element data were available for 11 freshwater lakes (81 samples), and the Waikato River, and 9 of its tributaries (62 samples). The Waikato River is the major river of the region and discharges into the Tasman Sea (Figure 1.4). More background information on the lakes and rivers sampled is in Appendix 2.5.

Freshwater data from rivers and streams within the Wellington and Marlborough regions were also made available by the Greater Wellington Regional Council and the Marlborough District council, respectively. However, this was for a more limited suite of trace elements and was used for comparison with the Waikato region data.

2.4 Groundwater samples

State of the Environment monitoring of groundwater for trace elements has rarely been carried out in New Zealand, although councils routinely carry out groundwater monitoring for other indicators of groundwater health. A recent extension of its groundwater monitoring programme to include trace elements was carried out by the Waikato Regional Council due to concerns about the fate of trace elements associated with agriculture, especially Cd and Zn (CWG 2008, Kim et al. 2008).

A total of 111 wells were sampled in the Waikato region as part of regional council groundwater monitoring programme (Hadfield 2013). A map of the sampling locations is provided in Appendix 2.5. The regional groundwater quality network was designed to represent the range of groundwater characteristics across the region. Sites were classified by land use. Appendix 2.6 provides detailed information on sampling protocols, collection, processing, and site background information.

Quality control measures are carried out in accordance with WRC's ISO 9001:2000 standards. These include procedures for the collection, transport and storage of samples. Samples were directly transferred to an IANZ-accredited laboratory for analysis. Back-up samples were held for two months until results had been verified by routine quality assurance procedures.

Groundwater data were provided by Auckland Council, and Taranaki and Greater Wellington Regional Councils, and are compared with the Waikato data. A wider suit of analyses were reported for the Wellington samples compared with the Waikato ones.

2.5 Sediment samples

Sediment data for a limited suite of trace elements from estuaries within Wellington, Southland and Tasman regions were supplied by the local authorities and was compared with Waikato region data. Within the Waikato region, 78 estuarine and 69 lake sediment samples were collected from Raglan (Whaingaroa), Kawhia, Tairua, Port Waikato and Firth of Thames estuaries, the discharge of the Waihou and Piako Rivers that are the Firth's major tributaries (Figure 2.1), and from 19 freshwater lakes (Figure 2.2) by engineers specialising in such sampling (Kim 2007, Appendix 2.7). Seven freshwater lakes had water sampled as well as sediments. Sampling in the southern Firth of Thames, Raglan (Whaingaroa), Aotea, Kawhia and Port Waikato occurred in 2008. In 2010 the sediments of Tairua were sampled. Additional sediments from the Firth of Thames Estuary were sampled in 2013 (Appendix 2.7). Sediment samples were collected from the mouths of the Waihou and Piako Rivers, and from a transect of an accretion mangrove forest site, from dry land to the ocean fringe, located by the Piako River mouth. Aerial photos show accretion has occurred at this site over the last

60 years (Swales et al. 2008). More background and location information on the estuaries, lakes and rivers sampled is in Appendix 2.5.

Figure 2.1: Aerial photo of the Firth of Thames and the catchment of the Waihou and Piako Rivers. Insert: detail showing the discharge of the Piako (upper centre) and the Waihou (upper right), (Waikato Regional Council).

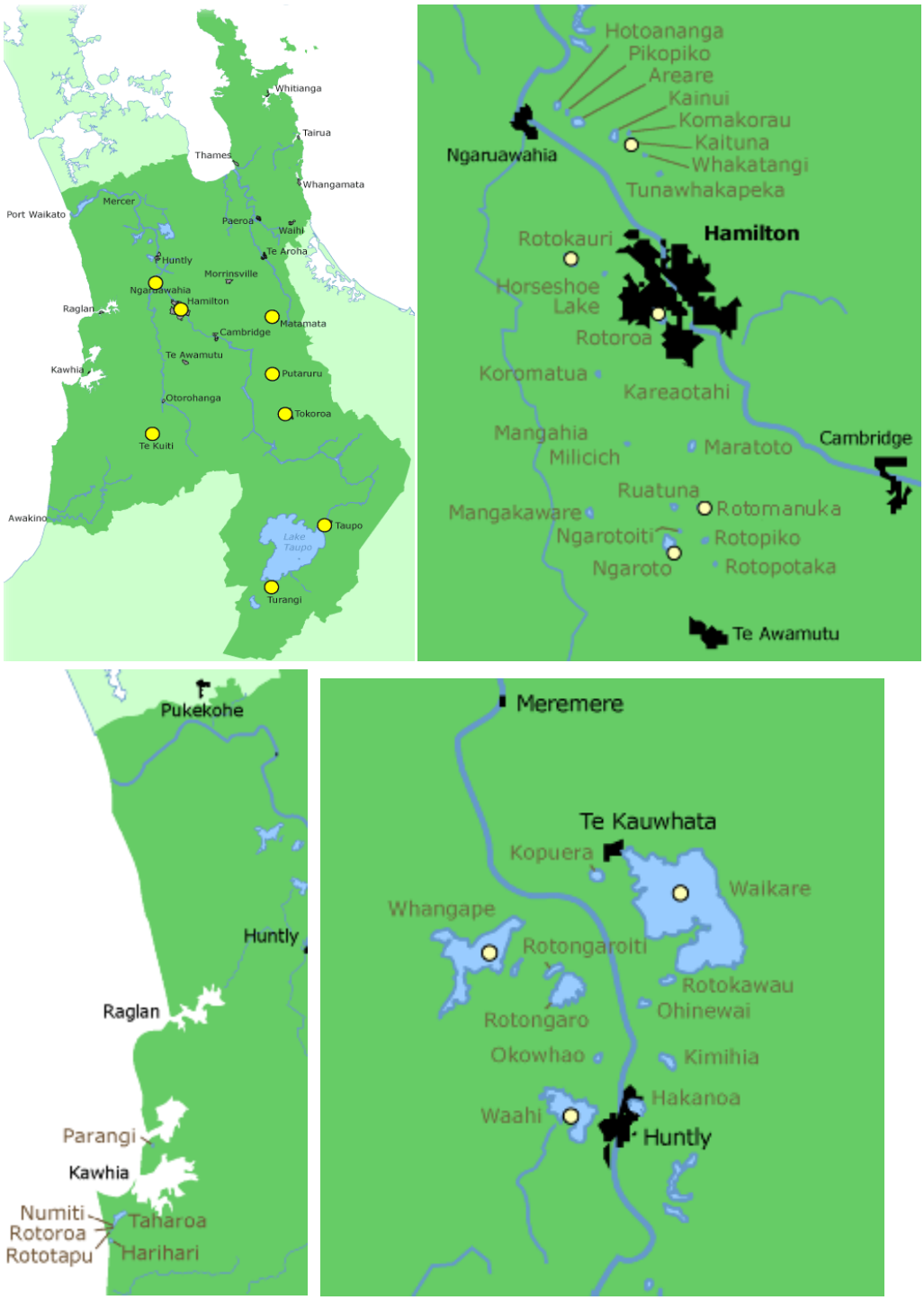

Figure 2.2: Maps showing an overview of the Waikato region (top left), the location of the peat lakes (top right), the west coast dune lakes (bottom left), and the riverine lakes (bottom right), (Waikato Regional Council).

For sediments, grab samples were taken from the upper 10cm of the lake bed as this zone provides the greatest exposure to lake-dwelling organisms. A petite ponar sediment grab sampler was used to collect the lake sediment samples. This sampler uses a spring-loaded pinch-pin to trigger the sampling jaws to close when the line slackens. When the sampler strikes the bottom, the tapered cutting edges penetrate the bottom sediment. The sampler closes once the pinch-pin has been released and the sampler is being retrieved. The sampler is equipped with mesh screens which allow water to flow through the sampler as it descends and this lessens the frontal shock wave thereby reducing surface disturbance. Both screens are covered with neoprene rubber flaps that close during retrieval to prevent any sediments being lost. A Russian peat corer was used to collect the estuarine sediments.

Once a sample was obtained, the contents of the sampler were deposited into a plastic tray and then sub-sampled into 2 x 250g glass soil jars supplied by Hill Laboratories. Each sample container was labelled with a unique sample identifier. All sampling equipment was rinsed and scrubbed clean with lake water between each sampling site.

2.6 Analytical methods

2.6.1 Soil Analysis

Soils were analysed using acid recoverable methodology following Kim & Taylor (2009) and data are presented in Appendix 1.2. A summary of the methods is supplied in Table 2.3. The same acid recoverable methodology was also used for soil, sediment and concretion samples. Some regions only analysed a restricted set of trace elements, e.g. F is only measured in the Auckland, Bay of Plenty, Waikato, Hawkes Bay, Wellington and Marlborough regions. In addition, cadmium data for one soil sample from under a recently sandblasted power pylon from the Taranaki region were provided.

Total elemental analysis was carried out on a subset of 256 Waikato region soil samples at the University of Waikato using XRF. Major and trace elements were determined on soil samples hand-ground in an agate pestle and mortar, and pressed into pellets for XRF analysis, using the Traces method on a polarizing energy-dispersive SPECTRO X-LAB 2000 instrument.

Table 2.3: Summary of methods used for soil and sediment analysis

Parameter	Method	Analysis
F_{total} (in solids)	Alkaline fusion of sample	Ion selective electrode (Adriano & Doner 1982)
Acid extractable elements	Nitric/hydrochloric acid digestion. US EPA 200.2.	ICP-MS

Element	Detection limit (mg kg^{-1} dry wt)
Acid extractable Al	10
Acid extractable Sb	0.04
Acid extractable As	0.2
Acid extractable Ba	0.02
Acid extractable Be	0.02
Acid extractable Bi	0.02
Acid extractable B	2
Acid extractable Cd	0.01
Acid extractable Cs	0.02
Acid extractable Ca	100
Acid extractable Cr	0.2
Acid extractable Co	0.04
Acid extractable Cu	0.2
Acid extractable Fe	40
Acid extractable La	0.02
Acid extractable Pb	0.04
Acid extractable Li	0.4
Acid extractable Mg	40
Acid extractable Mn	1
Acid extractable Hg	0.01
Acid extractable Mo	0.04
Acid extractable Ni	0.2
Acid extractable P	40
Acid extractable K	100
Acid extractable Rb	0.02
Acid extractable Se	2
Acid extractable Ag	0.02
Acid extractable Na	40
Acid extractable Sr	0.1
Acid extractable Tl	0.02
Acid extractable Sn	0.1
Acid extractable U	0.008
Acid extractable V	10
Acid extractable Zn	0.4

2.6.2 Water analysis

Groundwater and surface water from the Waikato River were analysed according to the methods in Table 2.4.

Table 2.4: Surface and ground water analysis methods and detection limits

Parameter	Method	Analysis
F_{total} (in waters)	APHA 4500-F	Ion selective electrode (Adriano & Doner 1982)
Dissolved metals	Laboratory 0.45µm filtered	ICP-MS APHA 3030B
Total metals	HNO_3 digestion. APHA 3030E	ICP-MS APHA 3125 B.

Element	Detection limit (mg m^{-3})
Total F	0.05
Total Al	5
Total Sb	0.1
Total As	0.25
Total Ba	0.06
Total B	20
Total Cs	0.01
Total Ca	100
Total Cr	0.2
Total Co	0.1
Total Cu	0.15
Total Fe	20
Total La	0.05
Total Pb	0.05
Total Li	0.05
Total Mg	100
Total Mn	0.5
Total Mo	0.1
Total Ni	0.15
Total K	100
Total Rb	0.1
Total Se	5
Total Ag	0.1
Total Na	100
Total Sr	0.06
Total Sn	0.1
Total U	0.05
Total V	0.05
Total Zn	1
Dissolved As	0.0011
Dissolved B	0.0053
Dissolved Ca	0.053
Dissolved Cd	0.053
Dissolved Cl	0.5
Dissolved Cu	0.00053
Dissolved F	0.021
Dissolved Fe	0.021
Disolved P	0.004
Dissolved Zn	0.0011

2.6.3 Sediment analysis

Sediment was analysed for an extended elements suite (33 elements to trace level using a total recoverable digestion as well as total organic carbon (TOC) at Hill Laboratories, the same methods used for soils (Table 2.3).

2.6.4 Quality control and assurance

Analysis was carried out at IANZ-accredited laboratories to quality standard NZS/ISO/IEC 17025:2005 which incorporates the aspects of ISO 9000 relevant to testing laboratories.

2.7 Statistical analysis

Multivariate factor analysis of the fertiliser and soils data were carried out using SPSS Statistics 7.0. Most data were not normally distributed so MANOVA and regression analysis by Spearman's rank correlations were used. Concentrations below detection limits were assigned a value of half the detection limit as long as >60% of the results were above the detection limit. After MANOVA confirmed that a factor was significant, detailed analysis of paired variables were carried out using pooled t-tests after data were log or square root transformed using Datadesk 6.0.

2.8 Priority analysis

2.8.1 The quantitative ranking model

A mass concentration approach is perhaps the simplest form of assessing risk posed by trace elements in fertilisers, and requires no knowledge of contaminant behaviour, no information on rate of fertiliser application and no information on the characteristics of the soil conceptually receiving the trace elements. This was the approach used by Molloy et al. (2005) as a screening test in deriving methodology for setting guidelines for contaminants in fertilisers in Australia. It assumes that deleterious impacts will occur if a trace element occurs in a fertiliser at a concentration greater to that of the receiving soil, or against some other specified concentration. The main problem with the mass concentration approach is the selection of reference concentration given the significant variation that occurs between different soil types and environments.

Mass balance modelling was considered as modelling may be used to predict the change over time in soil concentrations of each trace element. However, more detailed knowledge is needed of the fertiliser and other soil amendment inputs, trace element behaviour (partitioning, uptake, leaching, volatilisation, etc.), crop uptake and crop partitioning (to harvested portions). For common constituents, such modelling is possible but detailed and soil specific information is lacking for most trace elements. Thus, assumptions would need to be used in a mass balance model, which it was felt would make the model widely inaccurate. However, as scientific knowledge of trace element behaviour improves, such modelling is desirable in the future.

The quantitative ranking model used in this study is a simplification of the mass balance approach and is based on the relative importance, based on a score, of each element in relation to each of ten **factors**. These factors are the questions about the potential consequences to soil organisms, plant and human health and the wider environment. As each element is scored relative to the other elements in the analysis, the general trend is derived, rather than a soil concentration output.

The distinction between the types of consequences in five main categories were retained and the results of the assessment indexed back to environmental results, or used benchmarking based on known behaviour of one element, Cd. The five main consequences or effects linked to excess of an element are:

1. Enrichment in the fertiliser compared to the natural state of the receiving soil (1factor)
2. The likelihood of accumulation in soil (1 factor)
3. The likelihood of transfer across environmental compartments (2 factors; transfer to water; uptake by plants)
4. The likelihood of toxicity to soil organisms, plants and to people (3 factors for each of soil organisms, plants and people)
5. Radioactivity (3 factors; the proportion of each element naturally radioactive; the ICRP defined standard radiation weighting factor; the photoelectric effect)

2.8.2 Is the trace element present in environmentally significant quantities in fertiliser?

The first consideration was whether the trace element is present in environmentally significant quantities in fertiliser. This was derived by comparing the concentration of the trace elements in the fertiliser (Appendix 2.3) to that in background soil (Appendix 2.2), and results in a ratio (F:BG ratio). A trace element applied with fertiliser will only be of concern if it is present in large enough quantities to have an impact, i.e. several times that of background soils. Conversely, fertiliser to background soil ratios of <2.5 are not considered an environmental hazard (Kim et al. 2008). Elements likely present at >2.5 times background soil concentration were subject to further detailed assessment. This step acts as a screening test to reduce the number of trace elements for detailed assessment.

Levels of trace elements in background soils and fertilisers were derived. The median concentrations of trace elements for background soils of the world were drawn from 11 sources. Ten were from the literature and the other was from assessing soil quality monitoring data from NZ (Section 2.1 above). Total concentrations of trace elements in 1637 phosphate fertilisers, including inorganic fertilisers, phosphate rock, and fertilisers derived from organic materials, were compiled from 387 sources, including this study (Appendix 2.3, Section 2.2 above). Data were not found for all elements for all types of fertiliser.

Fertilisers were grouped according to type, outliers were excluded and the median concentration of each trace element calculated for each type of fertiliser. The median for each type of fertiliser was divided by the background soil value for each element to give the F: BG soils ratio. The greater the ratio the higher the potential for the element to accumulate in soils or be lost in leaching or taken up by plants. At the completion of this step, 27 trace elements with fertiliser to background soil ratios of greater than 2.5 remained for further assessment.

2.8.3 The likelihood of trace element accumulation in soil

The likelihood of accumulation in soil was assessed by benchmarking i.e. comparing soil-plant transfer factors and the sorption distribution coefficients (K_d) with a trace element known to accumulate due to fertiliser additions (Cd from superphosphate). The accumulation

of Cd from superphosphate additions in NZ is well documented (Taylor 1997a, Roberts et al. 1994).

In soil, trace elements interact with ligands in soil solution and with surface sites on the soil. K_d is the ratio of sorbed trace element concentration (expressed in mg/kg soil) to the dissolved metal concentration (expressed in mg/L water) at equilibrium (Allison & Allison 2005). As sorption can be rate-limiting to biodegradation, bioavailability, and transport of trace elements (Pignatello & Xing 1995), K_d can indicate the likelihood of accumulation in soil or migration to water. The lower the K_d coefficient, the greater the potential for the element to migration to water and the less likely it is to accumulate in soil.

K_d are influenced by multiple interrelated geochemical parameters and are site specific, e.g. due to interactions with pH, clay content, soil type, and metal concentration. Thus any element has a wide range of values, typically about 2.5 orders of magnitude (Sheppard et al. 2009a, USEPA & USDE 1999). However, U has a larger scatter of about 4 orders of magnitude from pH 4 to 9 due to its geochemistry. The hydrolysis of U under oxic conditions is dependent on the concentration of total dissolved U and dissolved hexavalent U can exist as polynuclear hydroxyl complexes. Under different geochemical conditions, U will adsorb to soil by less than 5 percent (very small K_d) or up to more than 95 percent (very large K_d) of its original dissolved concentration (USEPA & USDE 1999). In highly organic acid soils, such as found in NZ, U is expected to have an extremely high K_d, which is used in this study. However, if this priority assessment model is applied to soils with alkaline pH it is recommended that the low K_d value from USEPA & USDE (1999) be used.

The use of K_d expressions for sorption to natural particles in fate and transport models may be inaccurate due to slow kinetics, such as diffusion limitations (Pignatello & Xing 1995). However, despite the inaccuracies and the wide range of values, K_d coefficients are an indicator of the relative mobility of different trace elements. Estimates of K_d coefficients from 15 studies were correlated and median values determined (Appendix 2.8). Studies of contaminated sites were not included as higher concentrations of a metal will decrease the apparent K_d coefficient (due to a lowered affinity of the solid phase for the metal as it moves

toward saturation – Sauvé et al. 2000). If a trace element had a low K_d it had a higher likelihood of migrating from the soil and a lower likelihood of accumulating in the soil. U is a special case with both extremely high and low K_d for acid and alkaline soils respectively.

Plants inadvertently take up nonessential elements along with essential elements. If a trace element has high uptake into plants, it has a lower likelihood of accumulation in the soil. The likelihood of uptake into plants was assessed by ranking soil-plant transfer factors, also called transfer coefficients (TF). Estimates of TF from 24 studies were correlated and median values determined (Appendix 2.9). Transfer coefficients were defined for this exercise as the ratio between the content of the edible portion of the plant and that of the soil. The higher the soil/plant transfer coefficient, the greater the potential for the element to be taken up by plants. There were limited data on TF values for some trace elements including Lu, Tm and Yb, and data for these elements were from solely from Baes et al. (1984).

Cd is strongly enough bound to soil to accumulate in soil, but not so strongly bound that plant uptake is not significant. At standard rates of superphosphate use and at normal agricultural soil pH in NZ, at least 90% of Cd applied with superphosphate accumulates in the surface soils (Kim et al. 2008). Therefore, any element that shows (a) a high F: BG ratio (accumulation can only occur if a trace element is applied at greater than background concentrations, i.e. F: BG soils ratio >1), (b) a stronger soil binding capacity (K_d) and (c) a lower TF than Cd from the superphosphate group has a high probability of accumulating in soils. The result is a list of potential candidates that can be scored and compared to the score for Cd from superphosphate.

The model used to score the likelihood of accumulation was:

$$Accumulation\ \ score = \ (F{:}\ BG\ ratio - 1) * TF\ rank / \ Kd\ rank$$

The accumulation score is the relative likelihood of accumulation in soil of the different elements. The K_d and TF factors were ranked highest (rank 1) to lowest. Using rankings rather than actual K_d or TF factors allowed elements to be compared relative to each other and the

excessive influence of extreme K_d or TF factors were thus excluded. The greater the F: BG ratio, the greater the likelihood of accumulation as there is greater quantities of the trace element. Accumulation of elements with a Fertiliser: BG ratio ≤1 is impossible so one was subtracted from this ratio and the result then multiplied by the TF rank (the most likely to transfer, thus least likely to accumulate is ranked 1) and divided by the K_d rank (the most likely to accumulate ranked 1).

Each element in every fertiliser group was scored and an overall list of scores ranked (Appendix 2.10). Elements with no likelihood of accumulation, i.e. measured in a fertiliser group, but with F: BG soils concentrations ≤1 were identified as were elements that lacked concentration data.

2.8.4 The likelihood of trace element migration to water

The likelihood of migration to the hydrosphere was also assessed by ranking K_d values, but in reverse order from that used in calculating the likelihood of accumulation as the lowest K_d coefficients had the greatest likelihood of migration (Appendix 2.10). As there were 51 trace elements assessed in total, this was achieved mathematically by subtracting the K_d rank from 52 to give scores 1-51. The model used to score the likelihood of migration to water was:

$$Water\ risk\ score = (F{:}\ BG\ ratio - 1)/(52 - Kd\ rank)$$

The greater the F: BG ratio, the greater the likelihood of accumulation as there is greater quantities of the trace element. Accumulation of elements with a Fertiliser: BG ratio ≤1 is impossible so one was subtracted from this ratio and the result then divided by the reversed K_d rank (the most likely to migrate to water ranked 1).

2.8.5 The likelihood of trace element uptake by plants

The likelihood of migration of trace elements into the food chain via plants can be estimated by ranking the soil/plant transfer coefficients (Appendix 2.10).

$$Plant\ uptake\ risk\ score = (F{:}\ BG\ ratio - 1)/(TF\ rank)$$

The greater the F: BG ratio, the greater the likelihood of accumulation as there is greater quantities of the trace element. Accumulation of elements with a F: BG ratio ≤1 is impossible so one was subtracted from this ratio and the result then divided by the transfer factor rank (the most likely to taken up by plants ranked 1).

2.8.6 The impact to the health of soil organisms, plants and humans

Assessment of whether the trace element is significantly present in fertiliser to be of concern for the health of soil organisms, plants and humans was carried out. The toxicity of each element to microorganisms, plants and animals was assessed by comparing the ratio of the trace element concentration in fertiliser to soil guideline values for human health and ecological receptors published on the Environmental Guideline Value database (MfE 2013) to produce C: GV ratios. While MfE (2013) is a collation of the world literature and gives information on the confidence of each guideline, there was limited data for some elements (Appendix 2.11). Were there was limited data, information to inform a guideline was obtained from Alloway (1990), Paull et al. (1988) and Parks & Edward (2005). Where guidelines were below median background concentrations in soil or there were no guidelines, the background soil value was used.

2.8.7 The hazard from radioactive trace elements

Phosphate rock used for fertiliser is a major source of natural radioactivity due to both U and Th, and their decay chain daughters. A proportion of Rb is also naturally radioactive (Schulz 1965). Te is radioactive but its half life is so long that is is essentially stable over human lifetimes, so is placed in the stable elements. The proportion of radioactive isotopes for an element is the first consideration in this analysis of the hazard posed by radioactive elements.

Radiation from fertilisers includes alpha and beta particles as well as gamma rays. Gamma emissions have the highest penetrating power and emission length. From an external standpoint gamma emissions are the most hazardous. However, alpha emissions have such a high degree of ionization that if an emitted alpha particle was to contact living tissue it could cause nearly 20 times the damage of a gamma ray. Beta radiation emits electrons and has

intermediate penetrating power because beta electrons are smaller than alpha particles but larger than protons. Beta radiation can penetrate several millimetres into the skin. However, like alpha radiation, internal exposure to beta particles causes much more severe symptoms than external exposure (Was et al. 1994).

The hazard posed by different types of radiation has been standardised. The International Commission on Radiological Protection (ICRP) defined standard radiation weighting factors, independently of tissue type, to be used for risk and exposure assessment in radiology and the nuclear industry (ICRP 1991). The relative biological effectiveness (RBE) is the ratio of biological effectiveness of one type of ionizing radiation relative to another, given the same amount of absorbed energy. Different types of radiation have different biological effectiveness mainly because they transfer their energy to the tissue in different ways. Photons and beta particles have a low linear energy transfer coefficient. They ionize atoms in the tissue that are spaced by several hundred nanometres apart, along their path. In contrast, alpha particles leave a denser trail of ionized atoms in their wake, spaced about one tenth of a nanometre apart (i.e. less than one-thousandth of the typical distance between ionizations for photons and beta particles). The ICRP 1991 standard values for relative effectiveness for beta and gamma radiation are 1, while that for alpha radiation is 20 and these are used in this work.

The effect of radiation may be enhanced by the mass of heavy elements having affinity for DNA, which can result in anomalously high adsorption of natural background radiation (by the forth power of the atomic number Z^4) causing increased exposure to photoelectrons and recoil electrons (Busby & Schnug 2008).

The 3 factors assessing the hazard of radioactive trace elements in fertilisers used to supply P were amalgamated as a risk score, which was normalised to 2. It was calculated as the proportion of radioactive isotopes naturally abundant for each element and the overall scores. As the relative score is important, not the absolute numbers, they were normalised to the highest risk score (for U) to give the relative risk from radiation (Table 2.5). Not doing this normalisation resulted in too great an emphasis being placed on the hazard from radiation compared to the likelihood of chemical toxicity.

Table 2.5: Calculating the relative hazard from radioactive elements in P fertilisers.

Element	Proportion naturally radioactive (P)	Type of radiation	ICRP 1991 standard value (V)	Z^4	Hazard factor score $P*V*Z^4$	Relative hazard value	Hazard value (1+ relative risk)
All stable elements	0	none	0	n/a	0	0.00000	1
^{87}Rb	0.3	β^-	1	160000	49000	0.00003	1.00003
^{232}Th	1.0	α	20	65610000	1312000000	0.91620	1.91620
^{234}U	1.0	α	20	71640000	1432000000	1.00000	2.00000
^{235}U	1.0	α	20	71640000	1432000000	1.00000	2.00000
^{238}U	1.0	α	20	71640000	1432000000	1.00000	2.00000

2.8.8 The completed priority assessment model as applied to fertiliser derived trace elements

The rankings for accumulation, transfer to water and uptake by plants were added together as these are additive. For these 3 rankings, lower scores indicate higher likelihood of environmental impacts. Similarly, the likelihood of impacts to the health of soil organisms, plants and humans measured by the ratio of the trace element concentration in fertiliser to soil guideline values (C:Gv) are additive and these were multiplied by the radioactivity hazard score (which is effectively normalised to a maximum of 2). For these 4 values, the higher scores indicate greater likelihood of impacts to the health. Finally, the health scores (higher score = higher risk) were divided by the environmental risks (lower score = higher risk), multiplied by 1000 to give a whole number, to give an overall score, which was ranked:

$$Overall\ score = \frac{[\text{C: Gvsoil organisms} + \text{C: Gvplants} + \text{C: Gvhumans}] * \text{radioactive hazard value} * 1000}{[\text{rank accumulation} + \text{rank transfer to water} + \text{rank uptake by plants}]}$$

3. Results

3.1 Generating the data for the model

3.1.1 Background trace element concentrations in soil

The world background total trace element concentrations in soil were derived from the median of NZ soil quality monitoring data for natural background sites and from14 other studies of background concentrations in soils from 12 published sources (Appendix 2.2). Natural concentrations ranged over 5 orders of magnitude depending on the trace element (Figure 3.1). The trace elements with the highest median background concentrations were Ba (354 mg kg^{-1}), F (267 mg kg^{-1}) and Zr (259 mg kg^{-1}), while Ag (0.09 mg kg^{-1}) and Hg (0.10 mg kg^{-1}) had the lowest. Standard deviations were usually 50% or less except for Cd (116%), Cr (154%), Cu (139%), Ga (60%), Ge (606%), I (171%), Li (77%), Ni (235%), Se (108%), Ta (63%), V (1172%) and W (81%). It is expected these trace elements reflect local soil parent material. As the data were from published reputable sources or from soil quality state of the environment monitoring in NZ, the quality of the derived background trace element concentrations used in this study was assessed as moderate to high at a world scale. NZ data was generally lower than data from overseas, demonstrating data from the country of interest should be considered for use at a country scale.

3.1.2 Trace element concentration in P fertilisers

Median trace element concentrations in the different types of fertiliser were derived after collating 387 published literature sources, unpublished studies by Dr. Sylvia Kratz, Institut für Pflanzenbau und Bodenkunde, JKI and Dr. Geerd Smidt, EPI, and the author's unpublished XRF data (Taylor et al. 2014c, Appendix 2.3), a total of 5047 fertilisers. As the data were from published reputable sources or from reputable research organisations, the quality of the derived median trace element concentrations used in this study was assessed as moderate to high at a world scale. However, as individual countries do not have all sources of P fertiliser available, or choose to use particular sources for political reasons, concentrations of trace elements in fertilisers applied at the national scale and smaller may vary from this median, e.g. many mineral fertilisers analysed are no longer readily available on the world market as much of the more pure phosphate rock sources have been used up (Herring & Fantel 1993).

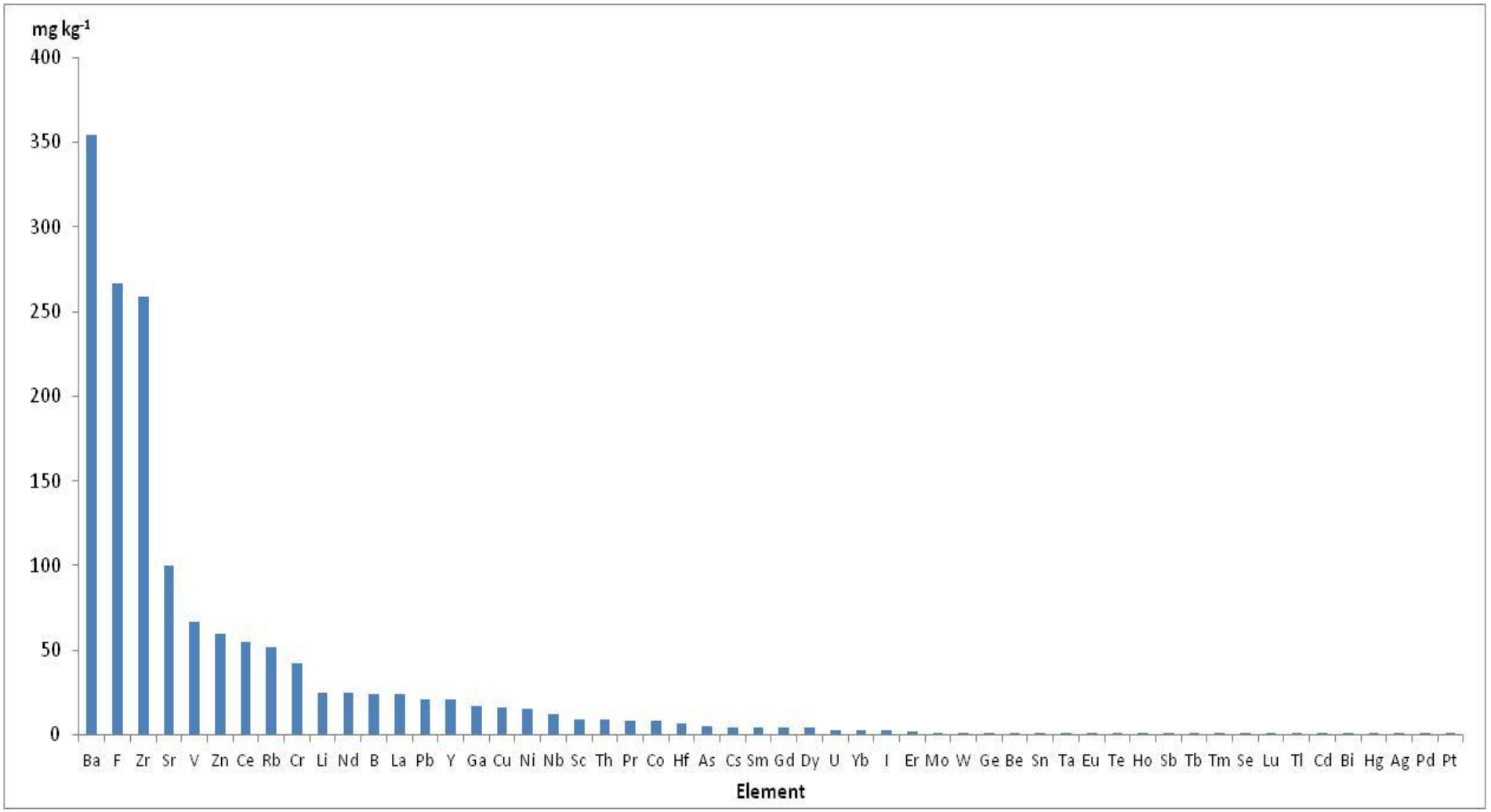

Figure 3.1: World background soil concentrations of 54 trace elements ordered from highest to lowest.

Trace elements with high fertiliser to background soil ratios were found in both inorganic and organic fertilisers (Appendix 2.10). Multivariate analysis of the data is presented in Figure 3.2. Principle Component Analysis (PCA) is a mathematical procedure widely used in exploratory data analysis to reduce data complexity, i.e. reducing dimensions and revealing relationships among data items. It can also be thought of as revealing the internal structure of the data in a way that best explains the variance in the data. Jeong et al. (2014) provide a detailed explanation of PCA. PCA is a method that projects a dataset to a new coordinate system by determining the eigenvectors and eigenvalues of a matrix. It involves a calculation of a covariance matrix of a dataset to minimise the redundancy and maximise the variance, i.e. finding the variances and coefficients of a dataset by finding the eigenvalues and eigenvectors. The covariance matrix is used to measure how much the dimensions vary from the mean with respect to each other.

The PCA of the fertiliser data set was carried out (Table 3.1, Figure 3.2). Although this is a relatively large dataset, few cases had all the data for all variables, which reduces the number of cases going into an analysis. Table 3.1 shows the varimax rotated matrix of components of main components with an eigenvalue > 1. Figure 3.2 gives the graphical representation of the first two main components of this matrix which explain 36% of the variability observed in the entire data set. Despite the limitation of reduced case numbers, the results of the PCA show the well known close connection between P, Ca, U and Cd. All four elements were highly loaded on the first principal component and in close proximity to each other in Figure 3.2. Also highly loaded on the 1st component and in close proximity to P, Ca Cd and U were Zn, Ni and Cr suggesting a possible connection between P and these three elements.

Table 3.1. Principal Component Analysis of element concentrations in fertilisers: varimax normalised rotated matrix of main components with an eigenvalue > 1.

	Component					
	1	2	3	4	5	6
% variance	19.2	16.9	12.6	9.1	6.9	5.7
Al	0.136	0.815	-0.095	0.119	-0.296	0.023
As	-0.010	0.010	-0.036	0.027	0.066	-0.939
B	0.129	-0.081	0.843	-0.118	0.031	0.065
Ca	0.529	0.111	0.025	0.095	-0.555	0.068
Cd	0.693	-0.094	-0.092	-0.039	-0.191	-0.103
Co	-0.083	0.111	0.905	-0.041	0.070	-0.024
Cr	0.831	0.042	-0.091	0.085	0.144	0.076
Cu	-0.137	0.051	-0.042	-0.911	0.108	0.067
Fe	0.048	0.830	0.116	0.067	0.052	0.022
Mg	-0.207	0.046	0.387	0.018	0.581	0.281
Mn	-0.119	0.851	0.007	-0.319	0.109	0.075
Mo	-0.122	-0.030	0.262	-0.651	-0.064	-0.099
Ni	0.616	0.085	0.093	0.069	0.240	0.016
P	0.597	0.010	0.386	0.001	-0.190	-0.015
Pb	-0.046	0.883	-0.010	0.024	-0.146	-0.094
Sr	-0.235	0.212	0.053	0.062	-0.740	0.190
U	0.861	-0.056	-0.021	0.026	-0.093	-0.037
Zn	0.525	0.012	-0.040	-0.635	0.076	0.119

Interesting, but without further interpretation, is that the typical pedogenetic elements Al, Fe and Mn along with Pb were loaded high on the 2nd principal component of the PCA, while B and Co are loaded high on the 3rd component, Cu, Mo and Zn were loaded high on the 4th component, Mg positively and Ca negatively loaded high on the 5th component and As negatively loaded high on the 6th component.

The median concentration for each element in each type of fertiliser (Section 2.8.2) was divided by the background soil value for each element to give the F: BG soils ratio (Table 3.3). The greater the ratio the higher the potential risk of accumulation in soils or increased

loss in leaching or uptake by plants. Those elements with the highest F: BG soil ratios for inorganic P fertilisers were Cd, F and U and these were highly correlated with P (Figure 3.2).

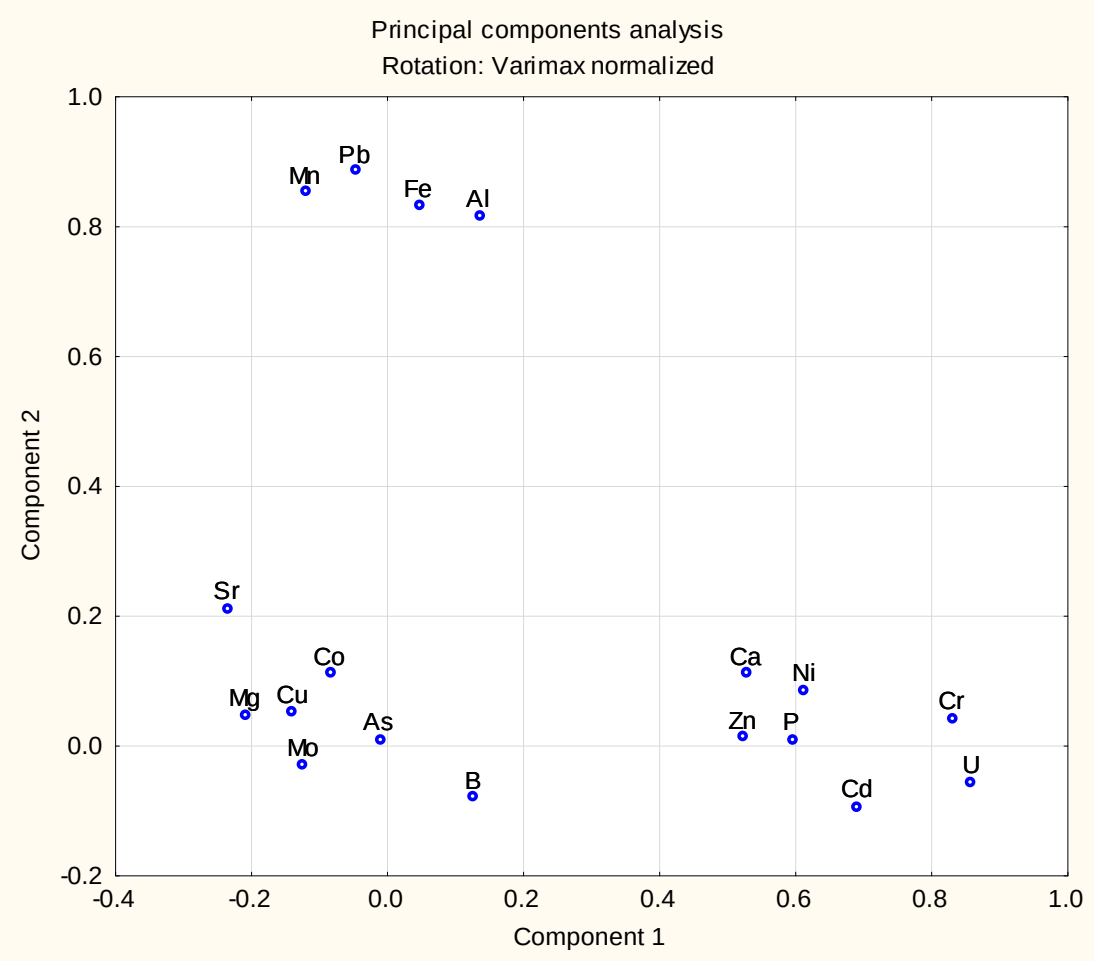

Figure 3.2: PCA of element concentrations of elements in fertilisers after varimax normalised rotation; display of first (P associated) and third (Al, Fe and Mn associated) components.

Conversely, fertiliser to background soil ratios of less than 2.5 are not considered an environmental risk (Kim et al. 2008). After comparing the F: BG soils ratios, 27 trace elements with F: BG soil ratios of greater than 2.5 remained for further assessment.

Table 3.2: Derived fertiliser: soil natural background (F: BG) ratios

	Derived from phosphate rock					Derived from organic materials					At least 1 F:BG
Element	AP/BG	SP/BG	TSP/BG	Blend/BG	RRP/BG	Piggery/BG	Poultry/BG	Cattle/BG	Plants/BG	Fish/BG	ratio >2.5
Ag	2	19	3	1	2	<1	-	1	1	3	Y
As	2	2	2	<1	2	<1	<1	<1	1	<1	N
B	6	7	19	9	21	1	1	1	<1	<1	Y
Ba	<1	<1	<1	<1	1	<1	<1	<1	<1	<1	N
Be	<1	<1	2	<1	1	<1	<1	<1	<1	<1	N
Bi	<1	<1	-	<1	<1	<1	<1	<1	-	<1	N
Cd	60	11	25	9	63	1	1	1	1	<1	Y
Ce	1	2	<1	1	5	<1	<1	<1	-	-	Y
Co	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	N
Cr	2	<1	2	<1	3	<1	<1	<1	<1	<1	Y
Cs	<1	<1	<1	<1	<1	<1	<1	<1	-	1	N
Cu	1	2	1	<1	1	12	5	1	1	<1	Y
Dy	2	3	2	2	-	-	-	-	-	-	Y
Er	2	3	2	2	-	-	-	-	-	-	Y
Eu	1	2	1	2	10	-	-	-	-	-	Y
F	71	55	79	86	116	-	-	-	-	-	Y
Ga	-	-	-	<1	-	-	-	-	-	-	N
Gd	1	3	1	2	25	-	-	-	-	-	Y
Ge	-	-	-	<1	-	-	-	-	-	-	N
Hf	-	<1	-	<1	<1	-	-	-	-	-	N
Hg	1	<1	<1	<1	<1	<1	<1	<1	<1	7	Y
Ho	1	2	1	2	-	-	-	<1	-	-	N
I	-	-	-	-	-	<1	<1	<1	-	-	N
La	1	2	1	2	8	-	1	<1	-	<1	Y
Li	<1	<1	<1	<1	<1	-	-	<1	-	<1	N
Lu	2	3	3	2	6	-	-	-	-	-	Y
Mo	2	2	4	2	4	2	2	1	1	<1	Y
Nb	<1	<1	<1	<1	-	-	1	-	-	-	N
Nd	1	2	<1	1	6	-	-	-	-	-	Y
Ni	2	2	2	<1	1	<1	<1	<1	<1	<1	N
Pb	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	N
Pr	<1	2	<1	1	-	-	-	-	-	-	N
Rb	<1	<1	<1	<1	<1	1	<1	<1	-	1	N
Sb	2	2	2	1	2	<1	<1	<1	1	<1	N
Sc	<1	<1	1	<1	1	-	<1	<1	-	-	N
Se	4	6	7	3	7	3	3	2	-	7	Y
Sm	1	4	1	1	9	-	-	<1	-	-	Y
Sn	<1	<1	<1	<1	<1	<1	<1	<1	-	-	N
Sr	1	11	8	3	14	<1	<1	<1	-	-	Y
Ta	-	-	-	<1	<1	-	-	-	-	-	N
Tb	2	5	2	2	12	-	-	-	-	-	Y
Te	-	-	-	<1	-	-	-	3	-	-	Y
Th	1	<1	<1	<1	<1	-	-	-	-	-	N
Tl	1	1	1	0	1	<1	<1	<1	-	<1	N
Tm	2	2	1	2	45	-	-	-	-	-	Y
U	18	11	32	10	26	<1	1	<1	-	<1	Y
V	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	N
W	-	-	-	<1	-	-	-	-	-	-	N
Y	3	5	3	4	6	<1	<1	<1	-	-	Y
Yb	2	2	2	1	3	<1	-	<1	-	-	Y
Zn	2	2	5	2	3	9	6	2	3	3	Y
Zr	<1	<1	<1	<1	3	-	-	-	-	-	Y

- = not determined

Table 3.3: Ratio of median trace element concentrations in fertilisers to soil guideline values for human health and ecological receptors used for agricultural soils.

	Derived from phosphate rock														
	AP/Guideline value			SP/Guideline value			TSP/Guideline value			Blended/Guideline value			RRP/Guideline value		
Element	Microbe	Plant	Human	Microbe	Plant	Human	Microbe	Plant	Human	Microbe	Plant	Human	Microbe	Plant	Human
Ag	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
B	5	5	0	6	6	0	16	16	0	8	4	0	17	10	0
Cd	5	4	12	1	1	2	2	2	5	1	1	2	6	4	12
Ce	1	0	0	2	0	0	0	0	0	1	0	0	4	0	1
Cr	1	0	2	0	0	0	1	0	1	0	0	0	1	0	2
Cu	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Dy	0	0	0	0	0	0	0	0	0	0	0	0	-	-	-
Er	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Eu	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
F	59	24	6	46	18	5	66	26	7	72	29	7	97	39	10
Gd	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0
Hg	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
La	0	0	0	1	0	0	0	0	0	1	0	0	4	0	0
Lu	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mo	0	2	0	0	1	0	0	3	0	0	1	0	0	3	0
Nd	0	0	0	1	0	0	0	0	0	1	0	0	3	0	0
Se	0	1	1	0	2	2	0	3	3	0	1	1	0	3	3
Sm	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0
Sr	0	0	0	2	1	0	1	1	0	0	0	0	2	1	0
Tb	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tm	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
U	5	11	2	3	7	1	9	19	4	3	6	1	8	16	3
Y	1	0	0	2	0	0	1	0	0	2	0	0	2	0	0
Yb	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Zn	1	2	1	1	2	1	3	4	1	1	2	1	2	3	1
Zr	0	0	0	0	0	0	0	0	0	0	0	0	3	3	3

AP = ammonium phosphates, SP = superphosphates, TSP = triple superphosphates, Blended = blended nitrogen phosphorous potassium fertilisers, RRP = Ground phosphate rock.
- no data

Table 3.3 continued: Ratio of median trace element concentrations in fertilisers to soil guideline values for human health and ecological receptors used for agricultural soils.

	Derived from organic materials														
	Piggery/Guideline value			Poultry/Guideline value			Cattle/Guideline value			Plants/Guideline value			Fish/Guideline value		
Element	Microbe	Plant	Human	Microbe	Plant	Human	Microbe	Plant	Human	Microbe	Plant	Human	Microbe	Plant	Human
Ag	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
B	1	0	0	1	0	0	1	0	0	0	0	0	0	0	0
Cd	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ce	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cu	2	2	3	1	1	1	0	0	0	0	0	0	0	0	0
Dy	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Er	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Eu	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
F	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Gd	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hg	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0
La	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Lu	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Mo	0	1	0	0	2	0	0	1	0	0	1	0	0	0	0
Nd	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Pb	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Se	0	1	1	0	1	1	0	1	1	0	0	0	0	3	3
Sm	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tb	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tm	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
U	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Y	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Yb	-	-	-	-	-	-	0	0	0	-	-	-	-	-	-
Zn	8	12	4	4	6	2	1	2	1	2	3	1	2	3	1
Zr	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

- no data

3.2 Overall priority ranking of trace element elements in P fertilisers

The quantitative priority ranking model is based on the relative importance of each element in relation to each of 10 factors (Section 2.8.1). The factors input to the model are:

1. Is the trace element present in environmentally significant quantities in fertiliser
2. The possibility of accumulation in soil (Section 2.8.3)
3. The possibility of transfer to water (Section 2.8.4)
4. The possibility of uptake by plants (Section 2.8.5)
5. The possibility of toxicity to soil organisms (Section 2.8.6)
6. The possibility of toxicity to plants (Section 2.8.6)
7. The possibility of toxicity to people (Section 2.8.6)
8. The proportion of each element naturally radioactive (Section 2.8.7)
9. The ICRP defined standard radiation weighting factor (Section 2.8.7)
10. The possibility of photoelectric effect (Section 2.8.7).

Whether the trace element is present in significant quantities in the fertiliser to have an environmental impact is assessed by deriving the ratio of the trace elements in the fertiliser to that in background soil (Section 2.8.2), and the ratio of the trace element concentration in fertiliser to soil guideline values for human health and ecological receptors (Section 2.8.6).

The ranking model was applied to each trace element in each fertiliser type and the scores for all the fertilisers were combined to create a global ranking list with rank 1 being the highest score and the greatest possibility of environmental and health impact. An example showing the highest and lowest environmental and health impact assessment components, overall score and final ranking, for F from RRP and Lu from BF is presented in Table 3.4. The model quantified those element–fertiliser combinations with possible impact to the environment and health from 1 – 193 (Table 3.5). There was no concentration data for 77 trace element/fertiliser group combinations and these could not be assessed.

Table 3.4: Final overall ranking: Example showing the highest and lowest environmental and health risk assessment components, overall score and finial ranking for F from RRP and Lu from BF. Rank 1 = greatest risk.

Fertiliser group	Element	Accumulation rank	Transfer to water rank	Plant uptake rank	Concentration/GV			Radioactive risk score	Overall score	Finial rank
					soil organisms	plant	Human			
RRP	F	2	10	102	97	39	10	1	1277	1
BF	Lu	78	103	11	0	0	0	1	0.07	107

There was a prevalence of trace elements from conventional inorganic P fertilisers in the top 25 ranks including trace elements from mineral fertilisers derived from P rock (AP, SP, TSP, BF, RRP), and alternate fertilisers derived from poultry and piggery products (Table 3.5). F from mineral fertilisers occupied the first 5 ranks, while Cd, U and B from mineral fertilisers were in the top 25 ranks. Other elements ranked in the top 25 included Zn from piggery and poultry products, Cu from piggery products, and Sr, La and Zr from RRP. Although the high rankings for Cd, F and U were anticipated, the high rankings for B, Sr and Zr were unexpected.

The elements may also be ranked by their highest position in Table 3.5. This gives a priority list of trace elements in fertilisers for Regional and Central Government authorities. Note that La can be used to represent the rare earth elements rather than measure each REE individually.

The list from highest priority to lowest is: F, Cd, U, B, Cu, Zn, La (and the other REE), Sr, Cr, Ag, Te, Mo, Se, Hg and Zr.

Table 3.5. Priority ranked fertiliser/element combinations from highest to lowest score

Fertiliser/element		Score	Rank	Fertiliser/element		Score	Rank	Fertiliser/element		Score	Rank
RRP	F	10402	1	Cattle	Zn	6.0	66	AP	Gd	0.4	131
Blended	F	4322	2	SP	Nd	5.8	67	AP	Zr	0.4	132
TSP	F	3402	3	AP	Se	4.9	68	AP	Yb	0.4	133
AP	F	2479	4	Cattle	Mo	4.0	69	AP	Er	0.4	134
SP	F	1595	5	Poultry	Se	3.9	70	Piggery	Sr	0.4	135
RRP	Cd	756	6	Blended	Sr	3.9	71	Poultry	Sr	0.4	136
TSP	U	679	7	Piggery	Se	3.9	72	SP	Tb	0.4	137
AP	Cd	661	8	SP	Cu	3.7	73	RRP	Lu	0.4	138
RRP	U	485	9	Blended	Se	3.7	74	AP	Sm	0.3	139
RRP	B	283	10	Blended	La	3.5	75	Plants	B	0.3	140
AP	U	257	11	Blended	Nd	3.3	76	SP	Eu	0.3	141
TSP	B	250	12	Plants	Cu	3.0	77	Blended	Yb	0.3	142
TSP	Cd	160	13	Cattle	B	2.9	78	TSP	Er	0.3	143
SP	U	131	14	AP	Cu	2.7	79	Plants	Ag	0.3	144
Blended	U	108	15	Fish	Hg	2.7	80	Cattle	Cr	0.3	145
Blended	B	103	16	Blended	Ce	2.6	81	Cattle	Sr	0.3	146
Piggery	Cu	78	17	SP	Sm	2.6	82	TSP	Dy	0.3	147
SP	B	76	18	Piggery	B	2.6	83	TSP	Gd	0.2	148
Piggery	Zn	62	19	AP	Ce	2.4	84	Blended	Eu	0.2	149
RRP	Sr	51	20	SP	Cr	2.4	85	TSP	Sm	0.2	150
AP	B	50	21	RRP	Eu	2.3	86	Piggery	Ce	0.14	151
RRP	Zr	50	22	Blended	Cr	2.0	87	Blended	Sm	0.13	152
SP	Cd	40	23	Plants	Cd	2.0	88	Cattle	U	0.13	153
Poultry	Zn	38	24	TSP	Cu	1.9	89	Blended	Ag	0.13	154
RRP	La	33	25	Cattle	Cu	1.8	90	Blended	Tb	0.11	155
RRP	Ce	33	26	Cattle	Se	1.8	91	TSP	Lu	0.11	156
RRP	Gd	32	27	RRP	Cu	1.7	92	SP	Lu	0.10	157
SP	Sr	32	28	Piggery	U	1.6	93	AP	Tb	0.09	158
TSP	Zn	27	29	Poultry	U	1.5	94	Cattle	Ag	0.09	159
Blended	Cd	26	30	SP	Gd	1.5	95	SP	Tm	0.09	160
RRP	Cr	24	31	RRP	Tb	1.5	96	AP	Eu	0.09	161
TSP	Sr	23	32	AP	Nd	1.4	97	AP	Hg	0.08	162
RRP	Nd	22	33	AP	La	1.4	98	TSP	Tb	0.07	163
RRP	Y	21	34	SP	Dy	1.3	99	Cattle	Sm	0.06	164
SP	Ag	20	35	TSP	Ag	1.3	100	TSP	Hg	0.06	165
AP	Cr	20	36	Fish	Ag	1.2	101	Poultry	Hg	0.06	166
Cattle	Te	20	37	Plants	Mo	1.2	102	AP	Lu	0.06	167
RRP	Mo	19	38	Poultry	La	1.1	103	Fish	B	0.06	168
TSP	Mo	18	39	Plants	Cr	1.1	104	Piggery	Y	0.06	169
Poultry	Cu	17	40	Cattle	Cd	1.1	105	Poultry	Y	0.06	170
RRP	Zn	15	41	Piggery	Cd	1.0	106	Fish	Cd	0.06	171
TSP	Cr	14	42	TSP	La	1.0	107	Poultry	Ce	0.06	172
SP	Y	14	43	Blended	Cu	1.0	108	AP	Tm	0.05	173
Fish	Zn	14	44	RRP	Yb	1.0	109	Blended	Tm	0.05	174
Plants	Zn	12	45	SP	Er	0.9	110	SP	Hg	0.05	175
TSP	Se	11	46	Poultry	Cd	0.8	111	RRP	Hg	0.05	176
Blended	Y	11	47	Fish	Mo	0.8	112	Piggery	Hg	0.05	177
RRP	Se	11	48	Blended	Dy	0.7	113	Cattle	Hg	0.05	178
Fish	Se	10	49	Poultry	Cr	0.7	114	Blended	Lu	0.05	179
Piggery	Mo	10	50	TSP	Nd	0.7	115	TSP	Eu	0.05	180
Poultry	Mo	10	51	Blended	Gd	0.7	116	TSP	Tm	0.04	181
AP	Mo	9.6	52	RRP	Ag	0.6	117	Cattle	Y	0.03	182
AP	Zn	9.3	53	Cattle	La	0.6	118	Piggery	Ag	0.02	183
SP	Se	9.0	54	TSP	Ce	0.6	119	Blended	Hg	0.013	184
Poultry	B	8.7	55	Blended	Er	0.6	120	Plants	Hg	0.013	185
SP	Zn	8.2	56	Blended	Zr	0.6	121	Cattle	Ce	0.010	186
RRP	Sm	8.2	57	TSP	Zr	0.6	122	Fish	Cr	0.010	187
RRP	Tm	8.0	58	Fish	Cu	0.6	123	Blended	Te	0.007	188
TSP	Y	8.0	59	AP	Ag	0.5	124	Cattle	Yb	0.003	189
SP	Ce	7.9	60	AP	Dy	0.5	125	Fish	Sr	0.0008	190
AP	Y	7.7	61	SP	Yb	0.5	126	Fish	La	0.0005	191
SP	Mo	7.5	62	AP	Sr	0.5	127	Fish	U	0.0003	192
Blended	Zn	6.9	63	Piggery	Cr	0.5	128	AP	Te	0.0000	193
SP	La	6.6	64	SP	Zr	0.5	129				
Blended	Mo	6.4	65	TSP	Yb	0.4	130				

3.3 Trace element concentrations in soil under different land uses in NZ

3.3.1 Trace element concentrations in NZ soils

Table 3.6 shows the PCA of element concentrations in New Zealand soils to give a general overview on the relation between the elements. There is a similar problem to that with the fertiliser data set that, although there are a large number of cases, due to missing data only a much smaller number of cases were suitable for PCA. The varimax rotated matrix of main components with an eigenvalue > 1 is displayed in Table 3.6. In addition, Figure 3.3 gives the graphical of the first, associated with Al, and third, associated with P, main components of this matrix, which explains only 14.9% of the variability, observed in the entire data set.

Despite the limitation of reduced case numbers, the results of the PCA show again the close connection between P and the elements U, Cd and F that was also observed in the PCA of the fertiliser materials (Section 3.1.2). All four elements are loading high on the third principal component (Table 3.3 and Figure 3.3). This result is an indication that the long term use of mineral fertiliser may have already overwhelmed the natural element pattern of NZ soils for these elements. In addition, N, Ca, pH and Zn also positively loaded on the third component, but less than P, Cd, F and U. This result suggests a lesser or indirect connection with P and, therefore P fertiliser. Although Ca is a natural major component of phosphate rock, where P fertiliser is applied it is likely that lime is also applied to neutralise acidity. However, lime contributes lesser amounts of trace elements than mineral P fertilisers and organic fertilisers (McLaughlin et al. 1996).

While P, Cd, F, N, Ca, pH and Zn are similarly slightly positively loaded on the first principle component, suggesting minor association with Al, U is highly positively loaded on this component. This result suggests two sources for U, one associated with P and the other with Al.

Interestingly, but without further interpretation, the other PCA components show the pedological relationship between Al and As, Bi, Cs, Hg, Mo, Se, Sn, and part of Li, U and V (component 1); between Mn and Ba, Cu, La, Ag, Tl, and part of Co and Zn (component 2); between Group I and II elements Ca, Mg, K, Na, Rb, Sr, and part of Li (component 4);

between Fe and Cr and Ni, and part of Co and V (component 5); between C and N (SOM) and part of Se (component 6); between Sb and Pb (component 7); and between soil pH and B and part Ca (component 8).

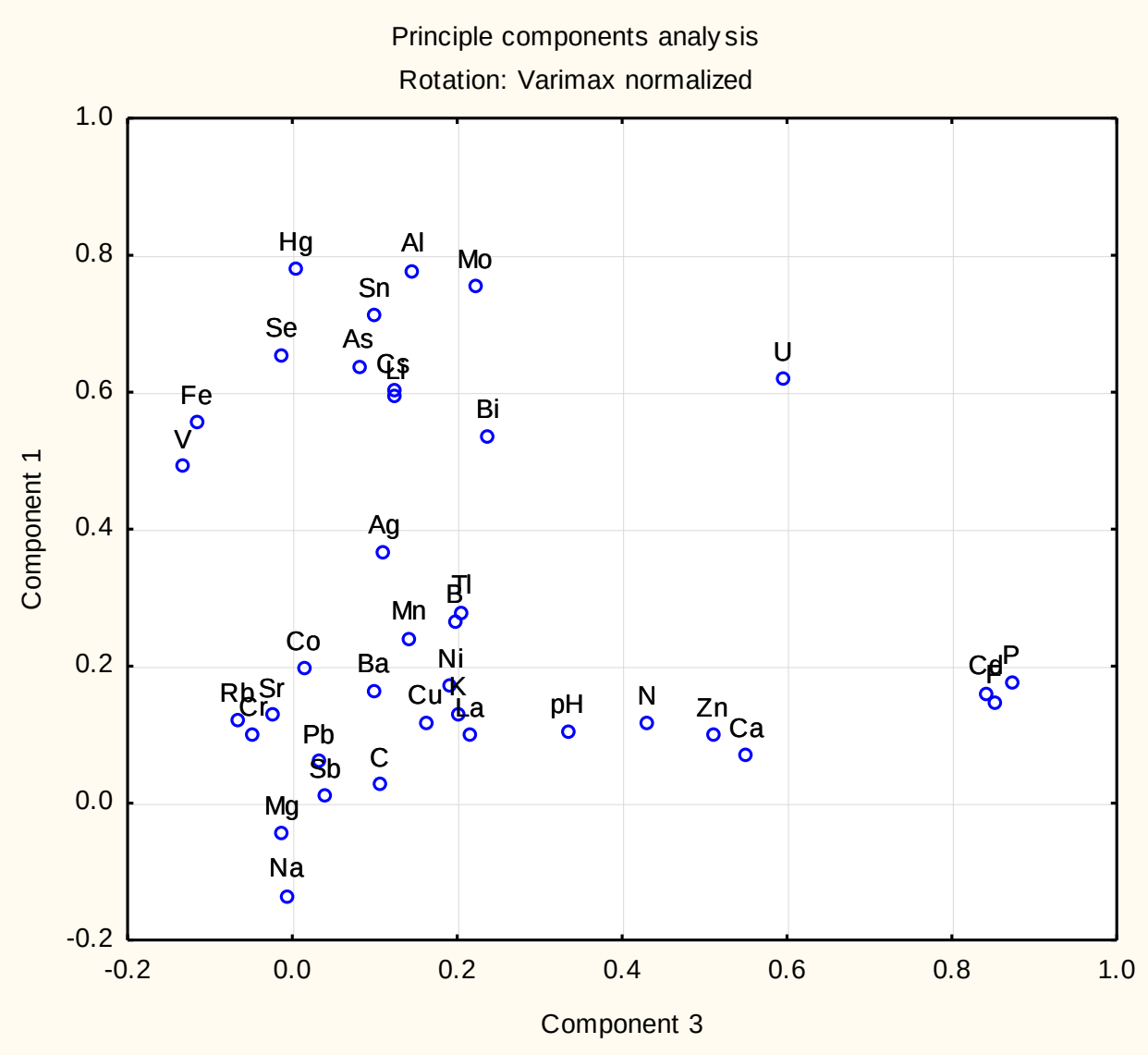

Figure 3.3: PCA of element concentrations in New Zealand soils after varimax normalised rotation; display of third (P associated) components and first (Al associated components)

The results of the PCA are consistent with conventional scientific wisdom on the behaviour of fertiliser trace elements Cd and U. These elements are associated with P content. Also associated with P content in soil, but to a lesser degree, were N, Ca and Zn.

Table 3.6: Principal Component Analysis of element concentrations in New Zealand soils: varimax normalised rotated matrix of main components with an eigenvalue > 1.

	Component							
	1	2	3	4	5	6	7	8
% Variance	11.5	4.2	3.6	2.4	2.1	1.7	1.6	1.2
pH	0.105	0.273	0.334	0.137	-0.026	-0.277	0.013	0.718
C	0.027	-0.027	0.106	-0.060	-0.075	0.921	-0.029	-0.079
N	0.117	0.121	0.431	0.040	-0.038	0.793	-0.024	-0.031
F	0.148	0.101	0.852	-0.105	-0.157	0.076	0.062	0.144
Al	0.778	0.442	0.146	-0.046	0.234	0.073	0.024	0.137
Sb	0.011	0.019	0.040	-0.001	-0.018	-0.013	0.995	0.021
As	0.638	0.005	0.081	0.423	0.007	-0.036	0.078	0.004
Ba	0.165	0.798	0.098	0.174	-0.010	-0.144	-0.048	0.020
Bi	0.536	0.046	0.237	0.064	0.047	0.022	0.010	-0.102
B	0.266	0.361	0.197	0.238	0.092	0.288	0.184	0.429
Cd	0.161	0.378	0.841	0.044	0.016	0.169	-0.004	0.063
Cs	0.602	0.133	0.123	0.239	-0.022	-0.377	0.050	-0.138
Ca	0.070	0.191	0.551	0.453	-0.017	0.122	-0.026	0.525
Cr	0.101	0.000	-0.047	-0.025	0.900	0.018	0.005	0.002
Co	0.197	0.549	0.013	0.326	0.406	-0.270	-0.010	-0.082
Cu	0.118	0.417	0.161	-0.012	0.232	0.079	-0.003	0.242
Fe	0.557	0.104	-0.116	0.096	0.716	-0.103	-0.004	-0.082
La	0.100	0.831	0.215	0.024	-0.091	0.291	0.033	0.124
Pb	0.061	0.053	0.032	-0.022	0.022	-0.034	0.989	0.013
Li	0.593	0.178	0.125	0.501	0.219	-0.072	-0.011	0.071
Mg	-0.043	-0.010	-0.013	0.884	0.187	0.018	0.012	0.104
Mn	0.241	0.846	0.141	0.047	0.102	-0.016	0.022	0.066
Hg	0.780	0.266	0.004	-0.090	0.166	0.167	-0.006	0.227
Mo	0.754	0.279	0.221	-0.047	0.267	0.244	0.040	0.062
Ni	0.171	0.105	0.192	0.201	0.858	0.041	0.013	0.082
P	0.176	0.176	0.872	0.114	0.033	0.183	0.031	0.105
K	0.130	0.172	0.200	0.778	0.089	-0.113	-0.022	-0.094
Rb	0.122	0.263	-0.067	0.664	0.056	-0.338	-0.050	-0.344
Se	0.655	0.115	-0.013	-0.118	0.175	0.443	-0.043	0.211
Ag	0.366	0.542	0.111	-0.004	0.065	0.392	0.008	0.157
Na	-0.135	-0.206	-0.007	0.604	-0.166	0.022	0.014	0.192
Sr	0.128	0.336	-0.025	0.662	0.037	0.268	-0.026	0.359
Tl	0.279	0.859	0.205	-0.037	0.035	-0.047	0.098	0.061
Sn	0.712	0.270	0.099	-0.084	0.268	-0.039	0.016	0.023
U	0.620	0.265	0.596	0.030	0.273	0.018	0.027	0.139
V	0.492	0.108	-0.133	0.004	0.754	-0.095	-0.013	-0.017
Zn	0.100	0.553	0.510	0.251	0.183	0.022	0.042	-0.041

3.3.2 Trace element concentrations by land use

Concentrations of P in non-fertilised soils (native and forestry) were considerably lower than those used long-term in agricultural and horticultural production (Table 3.7). Similar behaviour was seen for most trace element elements predicted to accumulate from P fertiliser additions (Cd, F, and U). The sample from under a power pylon measured 2.14 mg Cd kg^{-1} and was an outlier. The high result was attributed to Cd impurities in the Zn coating of the pylon. Regular sandblasting before recoating transfers Cd and Zn to the soil directly under the pylon.

However, some elements did not show accumulation in soil despite occurring in appreciable amounts in fertilisers. Ag was not significantly higher in fertilised soils compared to non-fertilised soils and B was significantly higher only in soil under kiwifruit orchards. Sources of high-Ag fertilisers are limited to mineral P fertiliser with moderate amount of Ag, so the magnitude of Ag application is low compared to Cd, F and U. Sources of B include timber preservatives and insecticides as well as fertiliser. There are also natural geothermal sources of B discharging to surface water that may be used for irrigation. It is conceivable that all 4 sources could be applied in kiwifruit orchards, allowing enrichment, even though B is highly mobile. Given its high mobility, soil B concentrations should decrease to background levels once additions cease.

Table 3.7. Median elemental concentrations in NZ soils under different land uses. Acid extractable data except total C, F, Te and Zr.

	Native			Forestry			Vineyard			Kiwifruit		
Element	Median (mg/kg)		n	Median (mg/kg)		n	Median (mg/kg)		n	Median (mg/kg)		n
P	311	a	83	347	a	93	1220	bd	5	1640	c	59
Total C	5.94	a	133	6.90	b	107	3.79	d	42	7.71	b	30
Ag	0.15	a	27	0.06	bc	42	0.23	abc	5	0.27	d	15
B	4.60	a	66	1.00	bc	64	2.25	ce	4	8.60	d	17
Cd	0.09	a	106	0.09	ab	119	0.17	c	42	0.89	d	30
Cr	9.5	abc	106	5.4	a	117	15.8	abc	42	10.0	ab	30
Cu	11.0	a	105	8.00	b	117	16.5	c	42	27.5	d	30
Total F	175	a	21	279	b	37	240	abd	2	570	e	15
Hg	0.12	a	85	0.05	b	95	0.05	c	11	0.11	ae	30
La	6.25	a	82	3.90	b	94	1.50	c	5	24.8	d	30
Mo	0.46	ade	82	0.27	b	93	0.23	ab	5	0.65	de	30
Se	<1			<1			<1			<1		
Sr	19.0	ae	82	12.1	b	94	13.0	abe	5	42.0	c	30
Total Te	1.8	a	24	1.9	a	30	-	-	0	2.1	a	12
U	0.56	ac	82	0.40	b	94	0.73	cd	5	1.96	e	30
V	54.0	a	67	27.5	b	64	52.0	abdg	5	45.0	adg	17
Zn	38.5	a	106	26.0	b	120	68.0	df	42	83.5	e	30
Total Zr	217	ab	24	207	a	30	-	-	0	213	-	12

Land uses with the same letter are not significantly different at p<0.05.
- = not determined

Table 3.7 cont.

	Vegetables			Other Horticulture			Dairy pasture			Pasture used for meat production		
Element	Median (mg/kg)		n	Median (mg/kg)		n	Median (mg/kg)		n	Median (mg/kg)		n
P	1620	c	38	1240	d	75	1810	e	202	1300	d	174
Total C	2.86	e	100	3.50	d	135	6.60	c	338	6.73	c	248
Ag	0.12	a	17	0.12	a	33	0.08	c	121	0.10	b	86
B	3.20	e	29	2.45	e	48	3.00	e	156	3.00	e	130
Cd	0.30	e	99	0.30	e	121	0.50	f	400	0.39	e	256
Cr	18.0	bc	101	11.3	abc	123	14.0	c	402	12.0	ab	217
Cu	19.3	e	98	70.0	fg	123	13.0	f	390	14.0	ag	244
Total F	401	cf	20	415	cf	28	475	f	126	365	cd	98
Hg	0.21	d	38	0.08	ce	75	0.10	ce	266	0.10	e	179
La	11.0	e	38	14.3	e	70	10.2	e	198	8.10	e	167
Mo	1.17	c	38	0.53	ade	70	0.58	ade	198	0.60	e	167
Se	1.30		38	<1			<1			<1		
Sr	19.5	ae	38	22.0	a	70	18.4	e	198	17.0	e	167
Total Te	1.6	a	16	2.4	a	21	2.1	a	154	1.9	a	95
U	2.35	f	38	1.22	d	70	1.57	e	202	1.30	d	174
Zn	70.0	f	99	62.0	d	121	61.0	d	401	47.0	g	256
Total Zr	312	b	16	229	a	21	218	a	154	253	a	95

Land uses with the same letter are not significantly different at p<0.05.
- = not determined

3.3.3 Comparing measured accumulation of trace elements in soil with estimated application in P fertilisers.

The soils data were simplified by placing them in one of two categories; fertilised and unfertilised. This method offered a simple overview of the effect of fertiliser without considering the impact of land use (Figure 3.4). It provided a method of analysis for elements where there were too few samples to carry out statistical analysis of its behaviour under different land uses.

The measured accumulation in soil of an element was calculated as the difference between its median concentration in NZ BG soil sites and the median concentration of all fertilised sites (Figure 3.4). However, the number of BG sites (36) is only a fraction of the number of fertilised sites. Also, the concentrations of many elements at BG sites are lower and closer to method detection limits, so could have higher measurement errors and should be used with caution. However, this NZ specific data is preferable to using the world BG value of Table 2.2 for this NZ – specific analysis. The measured accumulation in soil can be compared with the estimated total applied (Table 3.8); a simple mass balance. Accumulation in soil is assumed if the fertilised: BG ratio is greater than 1.1. Total XRF data from was used except for Cd and B, which are more accurately measured by acid extraction followed by ICP-MS. U data is presented as total and acid recoverable as explained below.

For fertiliser concentrations, NZ specific data was used, where available, as historic mineral P fertiliser in NZ was derived from the ancient guano deposits of Nauru, Ocean and Christmas Islands. During the 1950s and 1960s most SP in NZ was manufactured from Nauru and Ocean Island guano deposits (During 1972). During the late 1960s the exhaustion of the Ocean Island deposit and the ongoing depletion of the Nauru reserves resulted in using Christmas Island phosphate (During 1984). Blends containing about 50% Nauru and 50% Christmas Island were used to manufacture SP until 1987.

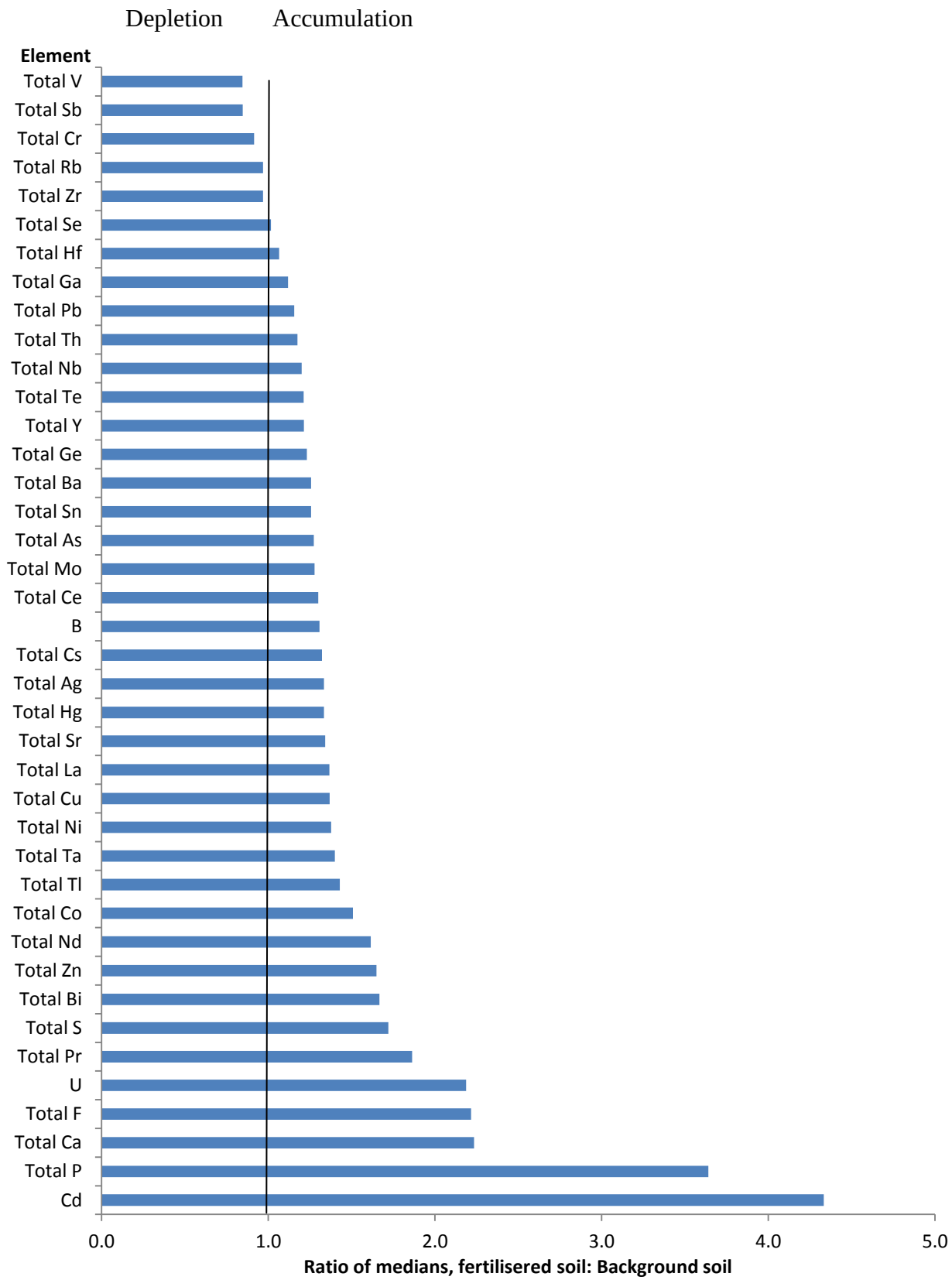

Figure 3.4: Accumulation or depletion of selected elements in NZ fertilised soils compared to natural background.

Table 3.8. Measured accumulation of fertiliser components and other trace elements in NZ soil compared with estimated amount applied in SP fertiliser, based on a 10 cm soil depth.

Element	Fertilised (mg kg^{-1})	Background (mg kg^{-1})	ratio	Measured accumulation (mg kg^{-1})	Estimated application as mg kg^{-1}	Unaccounted (mg kg^{-1})
Total P	2920	802	3.64	2118	3100	983
Total Ca	10390	4650	2.23	5740	6695	955
Total S	1545	898	1.72	647	3770	3123
Cd_{ar}	0.39	0.09	4.33	0.30	0.98	0.68
Total F	410	185	2.22	225	406	181
Total U	7.20	5.40	1.33	1.80	1.33	-0.47
U_{ar}	1.40	0.64	2.19	0.76	1.33	0.57
B_{ar}	3.40	2.60	1.31	0.80	5.79	4.99
Total Sr	106	78.8	1.34	26.9	34.7	7.78
Total Se	1.83	1.80	1.02	0.03	0.07	0.04
Total Bi	1.00	0.60	1.67	0.40	0.00	-0.40
Total Zn	100	60.4	1.65	39.2	4.10	-35.1
Total Nd	27.3	16.9	1.62	10.4	1.75	-8.65
Total Co	20.2	13.4	1.51	6.80	0.08	-6.72
Total Tl	2.00	1.40	1.43	0.60	0.01	-0.59
Total Ta	4.10	2.93	1.40	1.17	0.00	-1.17
Total Pr	23.9	12.8	1.86	11.1	0.43	-10.6
Total Ni	10.6	7.70	1.38	2.90	0.81	-2.09
Total Cu	22.3	16.3	1.37	6.00	0.88	-5.12
Total Hg	0.80	0.60	1.33	0.20	0.00	-0.20
Total Cs	12.1	9.15	1.32	2.95	0.01	-2.94
Total As	6.30	4.95	1.27	1.35	0.24	-1.11
Total Mo	2.30	1.80	1.28	0.50	0.10	-0.40
Total Ce	55.2	42.5	1.30	12.7	3.41	-9.31
Total Ba	435	346	1.26	88.9	1.49	-87.4
Total La	31.1	22.8	1.37	8.35	1.93	-6.42
Total Ge	1.60	1.30	1.23	0.30	0.00	-0.30
Total Sn	2.20	1.75	1.26	0.45	0.01	-0.44
Total Y	26.2	21.6	1.21	4.60	3.19	-1.41
Total Nb	11.4	9.50	1.20	1.90	0.03	-1.87
Total Te	2.00	1.65	1.21	0.35	0.00	-0.35
Total Th	13.8	11.8	1.17	2.05	0.05	-2.00
Total Pb	20.8	18.0	1.16	2.80	0.22	-2.58
Total Ag	0.80	0.60	1.33	0.20	0.06	-0.14
Total Ga	18.8	16.8	1.12	2.00	0.00	-2.00
Total Hf	8.50	7.98	1.07	0.52	0.00	-0.52
Total Zr	222	229	0.97	-7.10	0.54	7.64
Total Rb	55.7	57.5	0.97	-1.80	0.13	1.93
Total Cr	19.3	21.1	0.91	-1.80	0.97	2.77
Total Sb	1.10	1.30	0.85	-0.20	0.04	0.24
Total V	65.5	77.5	0.85	-12.0	2.10	14.1

These guano deposits contained relatively high Cd and U concentrations, about 48 and 60 mg kg^{-1} respectively (Syers et al. 1986, Appendix 2.3). However, NZ currently buys sedimentary P rock on the world market and Cd concentrations measured more recently averaged 23 and 22 mg kg^{-1} respectively (Taylor 2007b). F is typically much lower in guano (710 mg kg^{-1}) than in sedimentary P rock (15000 mg kg^{-1}). Christmas Island phosphate had quite low F content (1600 mg kg^{-1}), but Nauru phosphate had quite high content (22000 mg kg^{-1}), while the historic Ocean Island F content could not be found, but it is assumed to be like Christmas Island (Jenkins & Jackson 2014, Cronin et al. 2000, Piper et al. 1986, Syers et al. 1986, Doak et al 1965, Appendix 2.3). From the late 1980's NZ bought mainly Moroccan phosphate rock on the open world market. Cd, F and U concentrations measured more recently averaged 23, 15,000 and 22 mg kg^{-1} respectively (Taylor 2007b, Kim 2005, Cronin et al 2000).

SP is by far the most common fertiliser used in NZ (Hedley 2011, CWG 2008, Table 3.9). Assuming half the applied fertiliser to NZ soils had been from the guano deposits and half from phosphate rock, the average Cd, F and U concentrations in SP applied to NZ soils were 30, 12,500 and 41 mg kg^{-1}, respectively. For other elements, the median concentration for SP from the worldwide fertiliser elemental dataset was used (Appendix 2.3) due to lack of NZ – specific data. The total of each element applied was calculated using an average annual application of 400 kg ha^{-1} SP (Kim et al. 2008) over 65 years, with a soil bulk density of 0.8 t m^3 for the top 100 mm of the soil (Appendix 1.2).

The above assumptions may lead to inaccuracies in the estimated values but these should still be useful for statements at a national scale. Sample and measurement errors can also lead to inaccuracies in the measured values. Some elements, such as U and REES, have high measurement errors associated with them when analysed by XRF, e.g. measuring the same sample 26 times over the course of a year gave a CV of 25% for U, 50% for La, and 200% for Pr, while the standard reference material was on average twice its certified value for U. All U applied in P fertiliser has been shown to be acid soluble (Taylor & Kim 2008) and no other source of U is known for the NZ environment. Thus total U can be replaced by acid recoverable U for the analysis. However, it is not clear if there are other sources of REEs in NZ or if measurement error is the sole cause of the discrepancy for these elements.

The components of superphosphate, total P, Ca and S all showed considerable accumulation in fertilised soils compared to background, as did the known contaminants acid recoverable Cd, total F and U. However, for total P, Ca, S, F and acid recoverable Cd, the estimated application was considerable greater than the amount accumulated. This can be explained by movement of elements by soil organisms, ploughing and leaching below 100 mm, and by losses offsite in products. Similar behaviour was also seen for total Sr, Se and acid recoverable B and U.

For many other elements, the estimated application was less than the measured accumulation, which implies another source as well as P fertiliser.

3.3.4 Fertiliser regime patterns among land use forms in NZ

Investigation was limited by poor records of fertiliser use and the high turnover of farms with the new owner unaware of the previous fertiliser history. Farmer interviews showed change in farm ownership often lead to changes in fertiliser regime. Where fertiliser regime was continuous and farmers could supply fertiliser information, four fertiliser regimes could be compared. These were soils receiving ammonium phosphates (the salts of ammonium and phosphate), blended fertilisers (blended nitrogen, phosphorous – from phosphate rock, and potassium fertilisers), reactive rock phosphate (RRP, which is phosphate rock that is ground to very fine sand size that reacts with acids in the soil) and superphosphate (phosphate rock reacted with sulphuric acid).

Superphosphate was by far the most popular fertiliser applied (Table 3.9). Soils receiving blended fertilisers had the lowest V concentrations. RRP was used by organic farmers and soils receiving this fertiliser had the highest median concentrations for acid extractable P, Cd, Cr, Ni and Sr. However, these soils also had the lowest concentrations of total F, total Nd and total Ce. Organic farmers also used “organic mixtures” along with RRP. Soils receiving superphosphate had the lowest concentration of Ag.

Table 3.9: Soil P and trace element concentrations under 4 different fertiliser regimes in NZ. Acid extractable data except total Nd, Ce, Nb and F.

	Ammonium Phosphates		Blended fertilisers		RRP		Superphosphates	
Element	Median (mg/kg)	n	Median (mg/kg)	n	Median (mg/kg)	n	Median (mg/kg)	n
Total Nd	122 -	1	43.4 a	5	26.2 b	4	31.5 ab	73
Total Ce	86.7 -	1	79.6 a	5	49.8 b	4	60.1 a	73
Total Nb	10.2 -	1	13.0 a	5	12.7 a	4	11.4 a	73
Total F	390 a	4	430 bc	8	380 c	12	570 ab	170
Ag	0.18 ab	4	0.16 a	9	0.12 ab	12	0.09 b	213
As	6.90 a	4	6.80 a	9	6.45 a	12	5.00 a	213
B	6.00 ab	4	4.00 a	9	5.90 b	12	4.00 a	213
Cd	0.59 a	4	0.76 a	9	0.76 b	12	0.61 ab	213
Cu	28.0 a	4	16.2 a	9	18.6 a	12	17.7 a	213
Cr	11.3 a	4	10.0 a	9	15.0 b	12	9.00 a	213
Co	7.20 a	4	3.80 a	9	5.30 a	12	4.00 a	213
Hg	0.16 a	4	0.12 a	9	0.12 a	12	0.13 a	213
La	47.6 a	4	37.0 b	9	18.0 a	12	11.0 a	213
Mo	0.74 a	4	0.94 a	9	1.05 a	12	0.80 a	213
Ni	5.70 ab	4	5.50 a	9	6.60 b	12	4.90 a	213
Pb	11.9 a	4	12.3 a	9	14.0 a	12	11.0 a	213
P	1840 ab	4	1600 ab	9	2550 b	12	1720 a	213
Rb	9.35 ab	4	6.10 ab	9	9.05 b	12	6.85 a	213
Sn	1.55 a	4	1.70 a	9	1.28 a	12	1.32 a	213
Sr	23.0 a	4	16.0 a	9	32.5 b	12	18.9 a	213
U	2.10 ab	4	1.90 ab	9	2.15 b	12	1.83 a	213
V	52.5 ab	4	28.0 b	9	52.5 a	12	46.0 a	213
Zn	72.0 ab	4	62.0 ab	9	69.0 b	12	52.0 a	213

Fertiliser regimes with the same letter are not significantly different at $p<0.05$.

3.4 Trace element concentrations in sediments and waters in different regions of NZ.

3.4.1 Freshwater

Freshwater data for lakes in the Waikato region were collated according to lake type, while the data from the main Waikato River were one category and data from its tributaries another. Data from the Wellington region were able to be categorised by catchment land use. There were clear differences between regions, the different types of lake, rivers, and land uses (Tables 3.10-11). The variation in water elemental content for the Wellington region samples could be attributed to land use due to the geological similarity across the region, unlike the

Waikato Region, which had much more complex mixture of sedimentary and volcanic geological parent material as well as inputs of geothermal fluids.

Fertiliser associated elements will be considered in more detail in the discussion section but are commented on here briefly, while non-fertiliser associated elements are considered here for completeness.

Many of the elements in water samples from the Wellington region appeared associated with land use, e.g. low concentrations of B, Ca, K and Na were lowest in stream and river water samples from native land use catchments and higher in land used for forestry and pasture. These four elements are common constituents of fertilisers, limes and agricultural chemicals. The lithogenic element, Al, had similar concentrations across land uses, while Fe showed similar associations with the elements connected with productive land uses. In the absence of a source of Fe, this could be attributed to changes in the redox conditions of soils due to surface compaction reducing aeration. Thus, Fe^{3+} may be reduced to Fe^{2+} and mobilised. The prevalence and impacts of surface compaction in productive land has been described in soil quality monitoring reports for Wellington (Drewy 2013a) and scientific journal publications (Taylor et al. 2010).

In comparison, the catchments sampled in the Waikato region are dominated by productive land, mainly pasture. Another factor for the Waikato River is the input of geothermal water, both natural and from geothermal power stations, containing appreciable amounts of B, Li, Cs and As (Kim 2010, Timperley & Huser 1996). Median As concentrations were much higher in the Waikato River main stem and its tributaries than concentrations in lakes or rivers from the Wellington and Marlborough regions. However, median concentrations of B were highest in dune lakes surrounded by dairy land and the main stream of the Waikato River, likely reflecting the low capacity for soil to hold B from fertiliser additions as well as discharges of geothermal fluids.

Table 3.10. Elemental compositions of surface water samples from the Marlborough District, Waikato and Greater Wellington regions.

	Waikato Region					Greater Wellington Region			Marlborough
g m^{-3}	Puketirini dune lake	Ngaroto peat lake	Riverine lakes (n=9)	Waikato River Tributaries	Waikato River Main	Streams and rivers			Streams and rivers
Catchment dominant land use	Sheep/Beef	Dairy	Sheep/Beef/ Dairy	Forestry/ Sheep/Beef/ Dairy	Dairy	Pasture	Native	Forestry	
Al	0.008	0.255	0.087	0.040	0.015	0.026	0.029	0.027	-
Sb	<0.0002	<0.0002	0.0002	<0.0002	0.0006	-	-	-	-
As	0.001	0.001	0.001	0.035	0.023	0.0011	<0.0001	<0.0001	0.002
Ba	0.028	0.073	0.033	0.025	0.015	-	-	-	-
B	0.331	0.028	0.118	0.040	0.250	0.036	0.017	0.038	-
Cd	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.04	<0.04	<0.04	-
Cs	0.0001	0.0001	0.0002	0.0005	0.0080	-	-	-	-
Ca	20.0	14.3	14.2	9.8	6.7	23.9	57.1	26.4	-
Ce	<0.00005	0.0005	0.0003	0.0005	<0.00005	-	-	-	-
Cr	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	-
Co	0.0001	0.0003	0.0001	0.0005	0.0001	-	-	-	-
Cu	0.0003	0.0014	0.0009	0.0008	<0.0005	-	-	-	0.002
F	-	-	-	-	0.18	-	-	-	-
Fe	0.01	0.58	0.17	0.37	0.08	0.093	0.019	0.053	-
La	0.0001	0.0004	0.0001	0.0002	<0.00005	-	-	-	-
Pb	0.0001	0.0003	0.0001	0.0002	<0.0001	-	-	-	-
Li	0.026	0.002	0.004	0.008	0.086	-	-	-	-
Mg	10.6	4.4	4.2	4.0	2.7	-	-	-	-
Mn	0.004	0.083	0.007	0.064	0.004	-	-	-	-
Mo	0.0001	0.0001	0.0003	0.0001	0.0004	-	-	-	-
Ni	0.0006	0.0003	0.0005	0.0018	0.0003	-	-	-	-
N	0.22	-	2.20	0.43	0.34	-	-	-	-

- = not determined

Table 3.10 cont. Elemental compositions of surface water samples from the Marlborough District, Waikato and Greater Wellington regions

	Waikato Region					Greater Wellington Region			Marlborough
g m^{-3}	Puketirini dune lake	Ngaroto peat lake	Riverine lakes (n=9)	Waikato River Tributaries	Waikato River Main	Streams and rivers			Streams and rivers
Catchment dominant land use	Sheep/Beef	Dairy	Sheep/Beef/ Dairy	Forestry/ Sheep/Beef/ Dairy	Dairy	Pasture	Native	Forestry	
P	0.012	-	0.116	0.101	0.038	-	-	-	-
K	5.61	5.63	3.93	4.40	3.38	18.84	6.99	18.12	-
Rb	0.009	0.013	0.008	0.011	0.015	-	-	-	-
Se	<0.005	<0.005	<0.005	0.004	<0.005	-	-	-	-
Ag	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005	-	-	-	-
Na	20.4	11.7	17.6	17.4	19.5	16.7	9.0	19.8	-
Sr	0.25	0.09	0.09	0.07	0.04	-	-	-	-
U	0.00003	0.00003	0.00005	0.00003	0.00001	-	-	-	-
V	0.0005	0.0014	0.0013	0.0006	0.0010	-	-	-	-
Y	0.0007	0.0035	0.0014	0.0032	0.0015	-	-	-	-
Zn	0.008	0.255	0.087	0.040	0.015	0.002	-	-	0.003

- = not determined

Table 3.11. Water quality measurements of surface water samples from Lake Waahi, Waikato region, NZ.

Date	pH	P	N	Chlorophyll	Phycocyanin	Turbidity	B	Mo	U	V
		g m^{-3}	g m^{-3}	RFUB	RFUB	ntu	g m^{-3}	g m^{-3}	g m^{-3}	g m^{-3}
23/12/2008	8.8	0.08	1.10	-	-	-	-	-	-	-
23/02/2009	8.3	0.08	1.41	-	-	-	0.60	-	-	-
18/03/2009	-	-	-	-	-	-	0.59	-	-	-
9/04/2009	-	-	-	-	-	-	0.76	-	-	-
27/04/2009	8.2	0.10	1.31	-	-	-	-	-	-	-
20/05/2009	-	-	-	-	-	-	0.60	-	-	-
9/06/2009	-	-	-	-	-	-	0.45	-	-	-
24/06/2009	7.4	0.03	0.99	-	-	-	-	-	-	-
27/08/2009	7.9	0.03	1.19	-	-	-	-	-	-	-
27/08/2013	7.9	-	0.89	-	-	-	-	-	-	-
24/10/2013	7.8	0.04	1.29	-	-	-	0.34	0.0006	0.00015	0.0005
29/10/2013	-	-	-	-	-	-	0.35	0.0005	0.00014	0.0005
20/12/2013	8.3	0.09	1.19	-	-	-	0.43	0.0009	0.00028	0.0016
20/02/2014	-	-	-	21	80	99	0.80	0.0019	0.00090	0.0031
27/02/2014	8.7	-	3.10	-	-	-	-	-	-	-
23/04/2014	8.5	0.22	2.80	14	64	68	0.92	0.0024	0.00128	0.0025
13/05/2014	-	-	-	12	44	50	0.86	0.0022	0.00120	0.0023
26/06/2014	7.6	0.07	1.50	7	16	20	0.41	0.0007	0.00009	0.0005
3/11/2014	8.3	-	1.10	-	-	-	-	-	-	-
Not recorded	-	-	-	-	-	-	0.35	0.0008	0.00015	0.0004
Not recorded	-	-	-	-	-	-	0.64	0.0021	0.00088	0.0023
Not recorded	-	-	-	-	-	-	0.558	0.001	0.00052	0.0014

- = not determined

Median Fe and Mn concentrations were highest in peat lakes, probably reflecting the reducing environment associated with the high organic matter content of peat. The high organic matter content may also lead to the formation of soluble organic-metal complexes (e.g. with Cu and Zn) and is considered further in the discussion section.

Median P, Cd, F and U concentrations were very low, close to or below their detection limits. Riverine lakes had higher U concentrations, with one lake, Lake Waahi, having a particularly high average value of 0.0005g m^{-3}, ten times that of other riverine lakes. Further investigation showed B, Mo, V, pH as well as chlorophyll, phycocyanin and turbidity could be elevated when U levels were higher, consistent with algal blooms (Table 3.11).

Lake Waahi is a small shallow lake (maximum depth 5 m, surface area 5 km^2) at Huntly, NZ, and lies in an agricultural catchment. It often has well-developed chemical and thermal stratification, and heavy algal blooms (Chatman 1980). Algal blooms can have dramatic effects on water chemistry, most notably pH and DO. When algae remove CO_2 during photosynthesis they raise the pH by increasing the level of OH^-. High pH (> 8.0) can be an indicator of photosynthesis by large quantities of algae and it is not uncommon for pH to exceed 9 at Lake Waahi (Wells 1984, Chapman 1980).

At about the same time, Lakes Kimihia and Whangape also had elevated B, Mo, U and V but levels of U were considerably lower than concentrations at Lake Waahi (Appendix 3.1).

Samples from 5 sites along the Waikato River for a simplified suit of trace elements are presented in Table 3.12). These include its pristine discharge from Lake Taupo, below the discharge from geothermal power stations, below the only major city along its length (Hamilton City), and after flowing through farmland. Elevated As and Pb, and some Zn were associated with discharges from geothermal power stations and/or dairy farm land. Both farmland and urban discharges have been reported to contribute Zn to the Waikato River (Kim et al. 2008). Other trace elements measured, including the known mineral P fertiliser associated trace elements Cd and U, were below detection limits, possibly due to dilution as this water is sourced from the very pure Lake Taupo.

Table 3.12. Concentrations of N, P and selected trace elements at 5 sites along the Waikato River, NZ.

Site	Comment	N ($g\ m^3$)	P ($g\ m^3$)	As ($g\ m^3$)	Cd ($g\ m^3$)	Cr ($g\ m^3$)	Cu ($g\ m^3$)	Hg ($g\ m^3$)	Pb ($g\ m^3$)	U ($g\ m^3$)	Zn ($g\ m^3$)
Taupo	Pristine headwaters, As from natural geothermal inputs	0.08	0.006	0.010	<0.00004	<0.0005	<0.0002	<0.00008	<0.00005	<0.00002	<0.0005
Ohakuri Tailrace	Discharge from geothermal stations, dairy farms	0.21	0.022	0.031	<0.00004	<0.0005	<0.0002	<0.00008	0.00011	<0.00002	0.0015
Narrows Bridge	Intensive dairy farm land	0.42	0.032	0.025	<0.00004	<0.0005	<0.0002	<0.00008	0.00011	<0.00002	0.0030
Horotiu Bridge	Hamilton City discharge	0.44	0.032	0.025	<0.00004	<0.0005	0.0002	<0.00008	0.00008	<0.00002	0.0016
Tuakau Bridge	Waipa River and other major streams join the Waikato River Land use is mixed sheep/beef, dairy farm land and arable cropping Discharge to the sea	0.60	0.059	0.016	<0.00004	<0.0005	0.0007	<0.00008	0.00021	<0.00002	0.0023

Concentrations of Ca, Mg and Sr are high in peat lakes compared to other lakes, rivers and streams. The most likely sources of these three elements are inorganic P fertilisers, limes and lime amended organic fertilisers. Ca is a major component of all inorganic P fertilisers and lime, while Mg is elevated in P fertilisers and a major component of dolomite lime (Appendix 2.3). Lime is often added to acidic manures and composts to raise the pH. Sr has already been identified as a trace element elevated in inorganic fertilisers (Table 3.2).

Al, Fe, Mn were low in Waikato region peat lake waters, which may simply reflect the concentrations in the surrounding peat land. In addition, Fe and Mn may have been actively removed by Fe binding on peat sediment organics and microbially mediated Fe oxidation resulting in precipitation, while Mn would be retained as exchangeable Mn^{2+} (Henrot & Wieder 1990). Fe precipitation may also result in the coprecipitation of trace elements, such as As and Co.

Results of the principle components analysis of the Waikato lake waters set and the Waikato River and its tributaries set are displayed in Tables 3.13 – 14. The first principle component alone explained 33% and 31% of the variance for the lake and river sets respectively, although the elements associated with this factor were different for the two sets of data. For the lake waters, highly positively loaded on component 1 were Ca, Mg and Na along with B, Mo, Ni, Sr and U, which are associated with applications of fertiliser, limes and agricultural chemicals. Regression analysis using Spearman's Rank Correlation showed B, Mo and U to correlate with Na ($r = 0.780$, 0.732 and 0.565, respectively), while Ni and Sr were correlated with Ca ($r = 0.576$ and 0.840, respectively). Slightly positively loaded on component 1 were K along with Cu, and V, while the lithogenic elements Al, Fe and Mn along with As, Ba, Co, Cs, La, Pb, Rb and Zn were slightly negatively loaded on component 1. Li sat by itself being highly negatively loaded on component 2.

Interestingly, but without further interpretation, the other PCA components showed association with Mn, K and elements linked to inputs of geothermal fluids (Components 3,4 and 5 respectively).

Table 3.13. Principal Component Analysis of element concentrations in Waikato lake waters: varimax normalised rotated matrix of main components with an eigenvalue > 1.

	Waikato Lakes				
	Component				
	1	2	3	4	5
% variance	33.4	18.1	11.9	9.3	6.0
Al	-0.111	0.867	0.065	0.122	0.190
As	-0.050	0.262	0.052	-0.076	0.822
B	0.859	-0.254	-0.294	-0.062	-0.083
Ba	-0.111	0.492	0.409	0.676	-0.095
Ca	0.838	-0.067	-0.064	0.223	-0.298
Co	-0.062	0.038	0.862	0.116	0.209
Cs	-0.231	0.123	0.086	0.409	0.708
Cu	0.057	0.206	0.709	-0.312	0.064
Fe	-0.198	0.576	0.041	0.132	0.587
K	0.124	0.070	0.051	0.876	0.021
La	-0.289	0.780	0.167	0.136	0.283
Li	0.169	-0.575	-0.485	0.095	0.313
Mg	0.702	-0.180	-0.204	0.505	-0.128
Mn	-0.140	0.330	0.630	0.382	0.238
Mo	0.805	-0.068	0.223	-0.357	0.143
Na	0.917	-0.139	0.029	-0.147	0.116
Ni	0.557	-0.056	0.536	-0.190	-0.114
Pb	-0.113	0.888	0.064	0.090	0.206
Rb	-0.190	0.129	-0.022	0.836	0.304
Sr	0.905	-0.155	-0.202	0.093	-0.218
U	0.882	0.011	-0.011	-0.089	0.004
V	0.213	0.517	0.284	0.026	0.530
Zn	-0.235	0.084	0.636	0.336	-0.041

In comparison, PCA results for the Waikato River and its tributaries set were more complex. Elements associated with inputs of geothermal water, As, B, Cs, Li and Rb, were negatively loaded on component 1. The other components of the PCA showed Mn, Ca and Mg along with Co and Ni were highly positively loaded on component 2. Component 3 was associated with the elements U, V and Mo, component 4 with Al and Cu, La and Zn, component 5 with Na, B and Sr, component 6with Fe, Mn, Pb and La and component 7 with K, Rb and Ba. The lack of a pristine water sampling site to act as a control and the plausibility of P data makes

identification of the relative contribution of fertiliser associated elements problematic. The Lake Taupo discharge site (Table 3.12) showed how low natural levels of the restricted suit of trace elements are and this location could be used as a background control for a larger suit of trace elements in a future study.

Table 3.14. Principal Component Analysis of element concentrations in the Waikato River and its tributaries: varimax normalised rotated matrix of main components with an eigenvalue > 1.

	Waikato River and its tributaries						
	Component						
	1	2	3	4	5	6	7
% variance	31.1	15.5	13.1	11.2	7.3	6.5	4.7
Al	0.198	0.018	0.130	0.649	0.000	-0.455	0.228
As	-0.935	-0.181	0.038	-0.162	-0.038	0.115	-0.052
B	-0.308	-0.218	-0.114	-0.082	-0.882	0.044	-0.080
Ba	0.275	0.246	-0.328	0.456	-0.060	-0.111	0.622
Ca	0.404	0.600	0.037	0.090	-0.283	0.037	0.340
Co	0.110	0.855	-0.133	0.216	0.084	-0.241	0.263
Cs	-0.940	-0.180	-0.013	-0.154	0.002	0.182	0.042
Cu	0.297	0.268	0.225	0.765	0.168	-0.031	-0.194
Fe	0.330	-0.033	-0.018	-0.312	0.232	-0.731	0.094
K	0.096	0.344	0.063	0.212	0.050	0.002	0.885
La	0.177	0.252	0.429	0.428	0.073	-0.672	0.088
Li	-0.928	-0.178	-0.028	-0.181	-0.171	0.167	0.018
Mg	0.337	0.675	0.431	0.059	-0.330	0.101	0.189
Mn	0.226	0.594	-0.260	0.019	0.043	-0.563	0.283
Mo	-0.293	-0.052	0.883	-0.092	-0.117	0.158	-0.163
Na	-0.110	0.090	0.379	-0.297	-0.789	0.106	-0.021
Ni	0.115	0.925	0.155	0.078	0.051	0.103	-0.038
Pb	0.043	-0.075	0.003	0.233	-0.064	-0.839	-0.289
Rb	-0.473	-0.026	-0.141	-0.139	0.183	0.137	0.762
Sr	0.442	0.415	-0.067	-0.027	-0.754	0.003	-0.089
U	0.199	0.038	0.893	-0.054	-0.048	-0.019	-0.100
V	0.027	0.113	0.871	0.291	0.074	-0.260	0.100
Zn	0.107	0.070	-0.116	0.858	0.174	0.030	0.201

3.4.2 Sediment

Sediment data for lakes, collated according to lake type, and estuaries in the Waikato region were compared with estuarine sediments from other regions of NZ (Table 3.14).

Sediments from Waikato lakes were assessed for 22 major and trace elements (Appendix 3.1). Observations are focused on elements derived from fertilisers. Other observations are noted for completeness but not further discussed.

The data were compared to background soils values in Table 3.15. If particulate transport was occurring, element concentrations in lake sediments should reflect those in background soil for lithogenic elements, while fertiliser and agricultural chemical associated elements should increase with the intensity of farming.

Sediments from different lakes varied markedly in their Cd, P and Ca concentrations. All lakes sampled were influenced by farming, i.e. they received water that had passed through at least some farmland. Ca, P and Cd were elevated in the same lakes and appeared higher in lakes surround by intensive pastoral production, suggesting (mineral) P fertiliser and, for Ca, lime are the major sources (Appendix 3.1). The higher concentrations of these elements were in peat lakes surrounded by intensive dairy farms or in riverine or dune lakes with catchments used for meat production (Appendix 3.1). However, the U and total F concentrations were comparable to those for background soil, regardless of the surrounding land use, i.e. there was no relationship between fertiliser use and U or F content in lake sediments. Thus fertiliser applied U and F is adsorbed to soil and not transferred to lake sediment for this area. It appears particulate transport, overland flow and leaching are minor transport mechanisms for movement of trace elements to these lakes.

Zn tended to be higher in same lake sediments as Ca, P and Cd and is found in many fertilisers (Table 3.2) and agricultural chemicals.

As, B, Cs and Li concentrations were higher in sediment from volcanic/riverine lakes than in sediment from dune and peat lakes, and in background soils. The volcanic/riverine lakes were

formed by the ancient Waikato River, which contains water naturally elevated in elements from geothermal discharges. Although B may come from fertiliser applications, As, B, Cs and Li are also found in geothermal discharges (Kim 2010) and their close association suggests this is also the dominant source for B. Dissolved As in the Waikato River and removal can occur by adsorption onto Fe-oxide-suspended particulate matter (Webster-Brown & Lane 2005). Microbially mediated Fe oxidation and precipitation may also result in the coprecipitation of the other trace elements (Henrot & Wieder 1990) as described in section 3.4.1.

Lake sediments had elevated Pb concentrations compared to background soil. Some lakes have long been used for duck hunting and historic shot was made of lead. Another source was road stormwater, which contained lead from the burning of leaded petrol and lead weights used to balance vehicle tyres.

Fe, Cr, Ni and V were higher in dune lake sediments than in background soils but lower in riverine and peat lake sediments reflecting a geological influence. Titanomagnitite sands form the onshore beach and dune deposits in the area of the dune lakes contain relatively high concentrations of these elements (MED 2011).

Co tended to be higher in lake sediments compared to background soil and was accumulating despite it being relatively mobile (Table 3.15, Appendixes 2.12). Co is likely derived from animal supplements but could also be from Co-fertilisers, and was accumulating in these sediments, probably due to coprecipitation with Fe.

Estuarine sediments could be broken up into sediments from the southern part of the Firth of Thames and all other estuarine sediments. The southern Firth of Thames receives water with considerable concentrations of nutrients (Vant 2011), while waters on the west coast have lower levels of nutrients and sediments are baseline, near background, consistant with the intensity of farming within their catchments. Sediments from the southern Firth of Thames were higher in Al, B, Cd, Cs, Cr, Mg, Mn, P, Rb, Ag, Na and Sn than other estuarine sediments.

Similar to lake sediments, estuarine sediment data were compared to data from background soils (Table 3.15) as, in the absence of humans, estuarine sediment concentrations are likely to reflect those of background soils. P Cd, and B concentrations in estuarine sediments from the Southern Firth of Thames are higher than those in background soils and in sediments from other areas, suggesting that these are accumulating and likely due to land management in the contributing catchments of the Piako and Waihou Rivers.

Hg was elevated in sediments from riverine lakes and the Firth of Thames compared to background soil, but not in sediments from dune or peat lakes or from the west coast of the Waikato region or Wellington estuaries. Hg may be present in some fertilisers (Table 3.2).

Results of the principle components analysis of the Waikato lake sediment set are displayed in Table 3.16. Component 1 explained 28.4% of the variance and was associated with Al. Also highly positively loaded on component 1 were Ba, Cd, La, Mo, P, Ag, Tl, and Zn. Regression analysis using Spearman's Rank Correlation confirmed these elements were correlated with each other (Table 3.17). Also positively loaded on component 1 but not as high were Ca, Cu and U. Many of these elements are linked with the application of P fertilisers. U and Cu were also positively loaded on component 2, which was associated with K, Mn and organic carbon (OC). Spearman's Rank Correlation confirmed U was correlated with K.

When component 1 was plotted against component 2, another important fertiliser-linked element, F was shown as isolated from other elements, positively loaded on components 2, but highly negatively loaded on component 1 (Table 3.16). Interestingly, but without further interpretation, other trace elements associated with component 2 included As, Bi, Cs, Li, Rb, and Sn, while the other PCA components showed associations with Fe, Cs, Sb and Pb, As and Cs, B, Sn and Na for components 3-9 respectively.

Results of the principle components analysis of the Waikato estuaries set are displayed in Table 3.18. Component 1 explained 55.3% of the variance and was associated with Al, Mg, K and Na, while Ca was negatively loaded. Also highly positively loaded on component 1 were

Ba, B, Cs, Cr, La, Rb, Ag, Sn and U. The second component was associated with OC and Cd, P, Ni, Tl and U. Regression analysis using Spearman's Rank Correlation showed the controlling elements OC, Al and Mn to correlate with each other. Not surprisingly, elements that correlate with one of these controlling elements also correlate with the other two. Thus U correlates with both Al and OC and is highly loaded on both components 1 and 2 of the PCA. Similar results were seen for Cd and P.

Interestingly, but without further interpretation, other PCA components showed associations with a group of trace elements but no controlling element, Fe and Mn (components 3, 4 and 5, respectively.

Table 3.15. Median values of elements in sediment samples from the Waikato, Wellington, Tasman and Southland regions.

	NZ background soils	Waikato region lake sediments			Waikato region estuarine sediments							Estuarine sediments from other regions				
		Dune lakes	Peat lakes	Riverine/ lakes	Firth of Thames				West coast estuaries			Wellington		Tasman	Southland	
					Waihou	Piako	Appletree	Northern	Raglan	Aotea	Kawhia	Pauatahanui	Whareama	Motupipi	Jacobs	Freshwater
n		10	33	26	2	3	12	6	5	9	6					
OC	6.50	3.75	15.7	8.30	-	-	2.66	0.23	0.59	0.25	-	0.35	0.73	1.19	0.67	0.19
TN	0.36	0.40	1.25	0.77	-	-	0.30	0.07	0.10	0.08	-	-	-	-	-	-
C:N ratio	18.8	9.2	11.5	9.8	-	-	8.6	3.8	5.8	3.3	-	-	-	-	-	-
Al	23000	18600	36000	20800	33500	26150	28417	9301	10340	11089	17333	-	-	-	-	-
Sb	0.06	0.03	0.15	0.25	-	-	0.10	0.41	0.13	0.05	0.03	-	-	-	-	-
As	4.00	4.9	4.1	11.1	7.30	9.20	9.86	12.72	8.34	7.62	11.80	7.65	-	-	-	-
Ba	70	105	290	162	-	-	15	6	13	13	19	-	-	-	-	-
Bi	0.16	0.18	0.13	0.19	-	-	0.22	0.19	0.06	0.04	0.10	-	-	-	-	-
B	3.0	4.0	4.0	7.5	-	-	45.1	10.6	17.0	13.3	16.6	-	-	-	-	-
Cd	0.07	0.09	0.64	0.28	0.11	0.23	0.18	0.09	0.02	0.02	0.03	0.03	0.04	0.03	0.05	0.01
Cs	1.20	0.90	1.54	3.10	-	-	1.72	0.82	0.80	0.49	0.82	-	-	-	-	-
Ca	1440	3400	6600	3700	-	-	4217	18613	20756	9156	8817	-	-	-	-	-
Cr	9.1	21.5	7.8	8.0	30.8	24.3	34.8	14.9	14.4	12.4	12.9	9.5	9.1	35.0	9.0	3.3
Co	2.3	17.7	13.0	9.0	-	-	10.3	10.2	7.4	6.0	6.8	-	-	-	-	-
Cu	12.0	25.0	19.1	14.4	9.9	10.4	13.0	12.6	6.8	6.1	9.6	5.7	7.2	7.7	11.8	1.4
Total F	168	220	115	165	-	-	323					-	-	-	-	-
Fe	25000	72000	24000	27000	26500	19200	32083	24706	23100	23556	25333	-	-	-	-	-
La	6.7	11.6	21.0	11.5	-	-	13.7	7.2	9.1	6.4	10.7	-	-	-	-	-
Pb	9.5	14.1	21.0	18.0	26.5	29.5	47.6	24.3	6.1	3.8	7.7	9.0	7.7	22.3	4.3	0.7
Li	4.2	9.9	9.3	17.0	31.0	24.0	32.5	14.3	13.5	10.1	22.6	-	-	-	-	-
Mg	910	3000	850	1460	-	-	10375	5024	3778	2911	4383	-	-	-	-	-
Mn	240	895	360	899	-	-	2391	657	258	222	277	-	-	-	-	-
Hg	0.09	0.07	0.14	0.14	0.22	0.32	0.32	0.29	0.03	0.01	0.03	0.08	-	-	-	-
Mo	0.53	0.26	0.64	0.45	-	-	0.63	0.67	0.36	0.28	0.32	-	-	-	-	-
Ni	3.3	15.2	5.6	5.7	9.2	8.5	11.2	6.2	8.1	5.5	8.6	6.6	8.2	5.1	6.2	2.7

Table 3.15 continued. Median values of elements in sediment samples from the Waikato, Wellington, Tasman and Southland regions

	NZ background soils	Waikato region lake sediments			Waikato Region Estuarine sediments							Estuarine sediments from other regions				
					Firth of Thames				West coast estuaries			Wellington		Tasman	Southland	
		Dune lakes	Peat lakes	Riverine lakes	Waihou	Piako	Appletree	Northern	Raglan	Aotea	Kawhia	Pauatahanui	Whareama	Motupipi	Jacobs	Freshwater
P	290	1150	1300	655	-	-	809	316	529	529	643	136	388	565	341	171
K	480	815	560	808	-	-	-	1115	1396	990	1482	-	-	-	-	-
Rb	6.6	10.9	7.2	17.2	-	-	15.5	4.9	7.3	5.2	8.0	-	-	-	-	-
Se	3.00	<2	3.0	2.0	-	-	<2	<2	<2	<2	<2	-	-	-	-	-
Ag	0.08	0.06	0.17	0.08	-	-	0.84	0.11	0.05	0.01	0.02	0.07	-	-	-	-
Na	140	315	250	305	-	-	15758	5253	6622	4789	6533	-	-	-	-	-
Sr	16	29	56	39	-	-	61	116	112	82	100	-	-	-	-	-
Tl	0.14	0.10	0.59	0.23	-	-	0.08	0.08	0.06	0.04	0.06	-	-	-	-	-
Sn	1.10	1.14	1.00	1.30	-	-	1.47	0.43	0.46	0.42	0.67	-	-	-	-	-
U	0.71	0.87	0.69	0.85	-	-	0.82	0.37	0.60	0.42	0.53	-	-	-	-	-
V	50	255	42	34	-	-	45	43	63	85	59	-	-	-	-	-
Zn	30	90	146	89	92	104	124	81	48	38	44	45	40	36	38	7

- = not determined

Table 3.16. Principal Component Analysis of element concentrations in Waikato region lake sediments: varimax normalised rotated matrix of main components with an eigenvalue > 1.

	Waikato region lakes								
	Component								
	1	2	3	4	5	6	7	8	9
% variance	28.4	16.1	13.9	8.3	6.1	4.8	4.4	3.4	3.1
OC	0.154	-0.631	0.415	0.391	0.024	0.160	-0.161	-0.006	-0.299
Al	0.821	0.107	0.119	0.215	0.091	0.162	0.080	0.337	0.079
Sb	0.098	-0.044	0.026	-0.048	0.951	-0.075	0.024	0.003	-0.009
As	-0.091	0.174	0.106	-0.172	0.037	-0.916	-0.023	-0.032	-0.036
Ba	0.822	0.061	0.196	-0.105	0.117	-0.037	-0.028	-0.136	0.102
Bi	-0.053	0.701	0.421	-0.204	0.113	0.291	0.081	0.063	-0.279
B	-0.126	0.207	0.140	0.028	0.097	-0.042	0.901	-0.029	-0.075
Cd	0.877	-0.221	0.160	0.084	-0.043	0.050	0.036	0.132	0.035
Cs	-0.021	0.112	0.207	-0.585	0.017	-0.641	0.210	0.076	-0.051
Ca	0.432	-0.113	0.178	0.768	-0.003	0.170	-0.002	0.044	0.116
Cr	-0.328	0.127	-0.896	-0.076	0.024	0.193	0.039	0.017	-0.019
Co	0.204	-0.059	-0.886	0.101	0.113	-0.075	-0.072	-0.114	0.085
Cu	0.399	0.425	-0.158	0.066	0.497	0.450	-0.239	-0.034	-0.242
F	-0.650	0.480	-0.099	0.160	-0.136	0.102	0.224	0.073	0.038
Fe	-0.160	0.420	-0.789	-0.035	0.016	-0.048	-0.173	-0.111	-0.120
La	0.670	0.143	0.244	0.158	0.125	0.273	-0.086	0.210	0.286
Pb	0.104	-0.080	-0.148	0.046	0.934	0.030	0.076	0.004	0.061
Li	-0.054	0.915	0.081	-0.149	-0.012	-0.118	0.092	0.107	0.032
Mg	-0.344	0.781	-0.383	0.004	-0.048	0.153	-0.184	-0.068	-0.071
Mn	-0.150	0.754	-0.072	0.101	0.023	-0.233	-0.210	-0.243	0.143
Hg	0.153	0.045	0.418	-0.703	-0.062	-0.033	0.169	-0.001	0.145
Mo	0.579	-0.337	0.178	0.609	0.059	0.004	0.188	0.127	0.036
Ni	-0.272	0.614	-0.556	0.153	-0.042	0.211	0.298	-0.021	0.028
P	0.691	-0.078	-0.170	0.163	-0.150	0.062	-0.300	-0.005	-0.411
K	0.002	0.889	-0.069	-0.055	-0.093	-0.131	0.292	0.097	-0.027
Rb	-0.071	0.593	0.114	-0.446	-0.046	-0.316	0.499	0.129	0.021
Ag	0.621	-0.108	0.201	0.184	0.073	0.076	-0.085	0.693	0.082
Na	-0.431	-0.073	0.027	0.057	-0.015	-0.055	0.118	-0.040	-0.798
Sr	0.291	-0.030	0.338	0.691	-0.095	0.221	0.311	-0.025	-0.097
Tl	0.895	-0.200	0.187	0.119	0.040	-0.096	-0.064	0.060	0.088
Sn	0.090	0.110	0.050	-0.052	-0.022	-0.036	0.014	0.930	0.000
U	0.408	0.620	-0.064	-0.355	-0.065	0.003	0.180	0.335	0.156
V	-0.306	-0.088	-0.890	-0.126	0.063	0.212	-0.112	-0.004	0.001
Zn	0.743	-0.137	-0.239	0.233	0.320	0.113	0.068	0.077	0.253

Table 3.17. Spearman Rank Correlation of selected element concentrations in Waikato region lake sediments.

	OC	Al	Ba	Cd	Ca	Cu	F	Fe	La	Mg	Mn	Mo	P	K	Rb	Ag	Sr	Tl	U	Zn
OC	1.00																			
Al	0.32	1.00																		
Ba	0.13	0.46	1.00																	
Cd	0.56	0.72	0.55	1.00																
Ca	0.63	0.59	0.14	0.54	1.00															
Cu	0.11	0.45	0.20	0.26	0.31	1.00														
F	-0.43	-0.47	-0.62	-0.61	-0.30	-0.21	1.00													
Fe	-0.58	-0.18	-0.03	-0.38	-0.22	0.12	0.25	1.00												
La	0.19	0.81	0.40	0.60	0.49	0.41	-0.47	-0.23	1.00											
Mg	-0.66	-0.28	-0.30	-0.55	-0.30	0.04	0.51	0.50	-0.36	1.00										
Mn	-0.65	-0.24	0.18	-0.34	-0.36	-0.13	0.25	0.67	-0.08	0.35	1.00									
Mo	0.66	0.51	0.15	0.63	0.73	0.17	-0.49	-0.29	0.42	-0.42	-0.35	1.00								
P	0.42	0.64	0.33	0.60	0.48	0.64	-0.52	0.00	0.46	-0.29	-0.30	0.40	1.00							
K	-0.61	0.10	0.16	-0.16	-0.22	0.11	0.31	0.35	-0.01	0.55	0.52	-0.24	-0.08	1.00						
Rb	-0.64	0.06	0.20	-0.11	-0.46	-0.12	0.25	0.20	0.03	0.49	0.48	-0.35	-0.32	0.80	1.00					
Ag	0.48	0.85	0.52	0.91	0.60	0.32	-0.58	-0.36	0.73	-0.48	-0.36	0.66	0.60	-0.14	-0.08	1.00				
Sr	0.49	0.53	0.07	0.45	0.80	0.09	-0.18	-0.29	0.39	-0.16	-0.25	0.64	0.24	-0.13	-0.23	0.47	1.00			
Tl	0.46	0.69	0.66	0.89	0.48	0.20	-0.68	-0.23	0.65	-0.64	-0.18	0.53	0.56	-0.17	-0.14	0.84	0.34	1.00		
U	-0.52	0.26	0.34	0.10	-0.27	0.19	0.08	0.12	0.26	0.33	0.31	-0.17	-0.02	0.66	0.73	0.15	-0.21	0.09	1.00	
Zn	0.36	0.62	0.42	0.73	0.45	0.53	-0.54	-0.04	0.61	-0.43	-0.14	0.56	0.58	-0.17	-0.22	0.73	0.22	0.68	0.01	1.00

Table 3.18. Principal Component Analysis of element concentrations in Waikato region estuarine sediments: varimax normalised rotated matrix of main components with an eigenvalue > 1.

	Component				
	1	2	3	4	5
% variance	55.3	15.3	10.2	5.9	3.3
OC	0.191	0.945	0.082	0.130	-0.016
Al	0.918	0.263	0.147	-0.087	0.191
Sb	-0.428	-0.193	0.861	0.023	0.042
As	-0.155	-0.323	0.819	-0.339	0.115
Ba	0.576	0.496	-0.356	-0.276	0.126
Bi	0.432	0.058	0.860	0.048	0.149
B	0.938	0.125	0.054	-0.013	0.269
Cd	0.301	0.738	0.441	0.198	0.003
Cs	0.865	0.250	0.308	0.153	0.111
Ca	-0.745	-0.388	-0.058	0.195	0.157
Cr	0.849	0.304	0.336	-0.107	0.094
Co	0.253	0.422	0.703	-0.252	0.167
Cu	0.247	0.135	0.923	-0.099	-0.004
Fe	0.404	0.030	0.387	-0.777	0.053
La	0.832	0.394	-0.059	0.211	0.043
Pb	0.711	0.316	0.504	0.160	-0.138
Li	0.892	0.175	0.324	0.027	0.224
Mg	0.830	0.261	0.358	0.018	0.301
Mn	0.413	0.489	0.178	-0.006	0.638
Hg	0.368	0.105	0.835	0.149	-0.040
Mo	0.081	0.488	0.720	0.143	-0.058
Ni	0.350	0.887	0.167	-0.002	0.023
P	0.457	0.746	-0.026	-0.240	0.329
K	0.949	0.199	0.115	0.032	0.110
Rb	0.923	0.342	0.005	0.084	-0.013
Ag	0.843	0.313	0.283	0.111	-0.121
Na	0.703	-0.195	0.028	0.043	0.546
Sr	-0.711	-0.336	0.044	0.186	0.308
Tl	0.177	0.610	-0.035	0.582	-0.063
Sn	0.922	0.260	0.196	0.043	0.143
U	0.739	0.441	-0.021	0.291	-0.146
V	-0.306	-0.215	-0.163	-0.834	-0.090
Zn	0.556	0.374	0.659	0.069	-0.099

Table 3.19. Spearman Rank Correlation of selected element concentrations in Waikato region estuarine sediments.

	OC	Al	Ba	B	Cd	Ca	Cr	Cu	Fe	La	Mg	Mn	Hg	Mo	P	K	Rb	Ag	Na	Sr	Tl	U	Zn
OC	1.00																						
Al	0.68	1.00																					
Ba	0.57	0.56	1.00																				
B	0.78	0.84	0.46	1.00																			
Cd	0.66	0.66	0.06	0.63	1.00																		
Ca	-0.79	-0.72	-0.46	-0.68	-0.54	1.00																	
Cr	0.69	0.82	0.22	0.81	0.77	-0.63	1.00																
Cu	0.34	0.66	0.15	0.49	0.76	-0.40	0.81	1.00															
Fe	0.16	0.63	0.19	0.58	0.46	-0.40	0.78	0.71	1.00														
La	0.73	0.81	0.56	0.80	0.60	-0.62	0.71	0.48	0.48	1.00													
Mg	0.64	0.84	0.23	0.81	0.82	-0.57	0.91	0.80	0.77	0.71	1.00												
Mn	0.73	0.71	0.12	0.71	0.77	-0.50	0.85	0.76	0.72	0.64	0.91	1.00											
Hg	0.41	0.60	-0.04	0.57	0.88	-0.47	0.81	0.83	0.60	0.59	0.84	0.79	1.00										
Mo	0.44	0.49	-0.03	0.38	0.79	-0.33	0.67	0.75	0.43	0.37	0.62	0.59	0.75	1.00									
P	0.83	0.69	0.48	0.60	0.37	-0.59	0.54	0.44	0.44	0.54	0.52	0.59	0.26	0.24	1.00								
K	0.72	0.86	0.37	0.93	0.74	-0.68	0.86	0.58	0.63	0.84	0.88	0.75	0.71	0.49	0.49	1.00							
Rb	0.74	0.83	0.46	0.93	0.65	-0.74	0.80	0.49	0.55	0.89	0.81	0.69	0.64	0.35	0.55	0.94	1.00						
Ag	0.69	0.68	0.01	0.68	0.86	-0.55	0.84	0.73	0.59	0.71	0.86	0.84	0.91	0.70	0.42	0.81	0.75	1.00					
Na	0.29	0.73	0.37	0.72	0.43	-0.30	0.63	0.46	0.53	0.60	0.69	0.47	0.47	0.31	0.26	0.73	0.64	0.51	1.00				
Sr	-0.64	-0.56	-0.32	-0.61	-0.47	0.90	-0.57	-0.28	-0.44	-0.55	-0.47	-0.40	-0.45	-0.30	-0.36	-0.67	-0.68	-0.49	-0.21	1.00			
Tl	0.62	0.50	0.15	0.57	0.76	-0.41	0.57	0.41	0.22	0.66	0.59	0.61	0.64	0.52	0.20	0.67	0.63	0.67	0.33	-0.44	1.00		
U	0.81	0.70	0.33	0.74	0.69	-0.59	0.67	0.41	0.30	0.80	0.62	0.51	0.55	0.56	0.49	0.78	0.80	0.69	0.45	-0.54	0.65	1.00	
Zn	0.66	0.68	0.09	0.67	0.84	-0.56	0.90	0.84	0.75	0.63	0.88	0.90	0.88	0.71	0.48	0.78	0.70	0.88	0.42	-0.56	0.65	0.59	1.00
	OC	Al	Ba	B	Cd	Ca	Cr	Cu	Fe	La	Mg	Mn	Hg	Mo	P	K	Rb	Ag	Na	Sr	Tl	U	Zn

3.4.3 Absorption coefficients

There were seven lakes in the Waikato region that had data for both sediment and water trace element concentrations (Appendices 3.1), which allowed an estimation of K_d values. The medians of the estimated K_d values were compared with the soil:water K_d values (Appendix 2.8), and the sediment:water K_d values of IAEA (2010) and the freshwater and marine values of Sheppard et al. (2009) (Table 3.20). The median sediment: water K_d values estimated in this work were generally lower, but within the expected range of values (IAEA 2010, Sheppard et al. 2009).

There was a power relationship between the estimated sediment:water K_d values and the soil:water K_d values (Figure 3.5). Some sediment:water K_d values were higher than soil:water K_d values, probably reflecting differences between the terrestrial and aquatic environments, e.g. redox, pH. Proportionally, elements with the lowest K_d values had greater increase than elements with the highest K_d values. Of particular note were Zn and Co, which had much higher K_d values in lake ecosystems than in soil ecosystems, i.e. Co and Zn were proportionally more highly partitioned onto sediment in lake systems than onto soil, suggesting lake sediments could be a sink for these elements, compared to land. Elevated Co concentrations in lake sediments were reported in section 3.4.2.

Mo, Mn and V were also more highly partitioned onto sediment in lake systems than onto soil, but to a lesser extent than Co and Zn.

On the other hand, Rb and B were proportionally more lowly partitioned onto sediment in lake systems than onto soil, suggesting lake sediments have less affinity for sorbing these elements than soil.

Table 3.20. Average of estimated sediment: water K_d values from 7 lakes and calculated soil: water K_d values compared with values from IAEA (2010) and Sheppard et al. (2009).

	K_d (L kg^{-1})				
	Median K_d sediment: water	K_d soil:water	IAEA 2010 sediment	Sheppard et al 2009 freshwater sediment	Sheppard et al 2009 marine sediment
Al	16111	15150	-	-	-
Sb	122	346	5000	4100	1100
As	788	713	-	-	-
Ba	544	210	2000	-	-
B	4	88	-	-	-
Cs	1820	2000	29000	17000	540
Ca	28	77	-	-	-
Co	6685	631	-	-	-
Cu	1601	943	-	-	-
Fe	26485	14250	-	160000	2900000
La	13764	7200	-	300000	-
Pb	21298	9600	-	130000	180000
Li	178	325	-	-	-
Mg	24	300	-	-	-
Mn	10742	2050	79000	28000	48000
Mo	188	75	-	1100	-
Ni	1979	1259	-	1500	17000
K	21	242	-	-	-
Rb	207	6300	-	-	-
Na	2	19	-	-	-
Sr	38	106	1200	480	5
U	1894	3981	-	15000	860
V	2627	501	-	-	-
Zn	6891	530	-	-	-

- = not determined

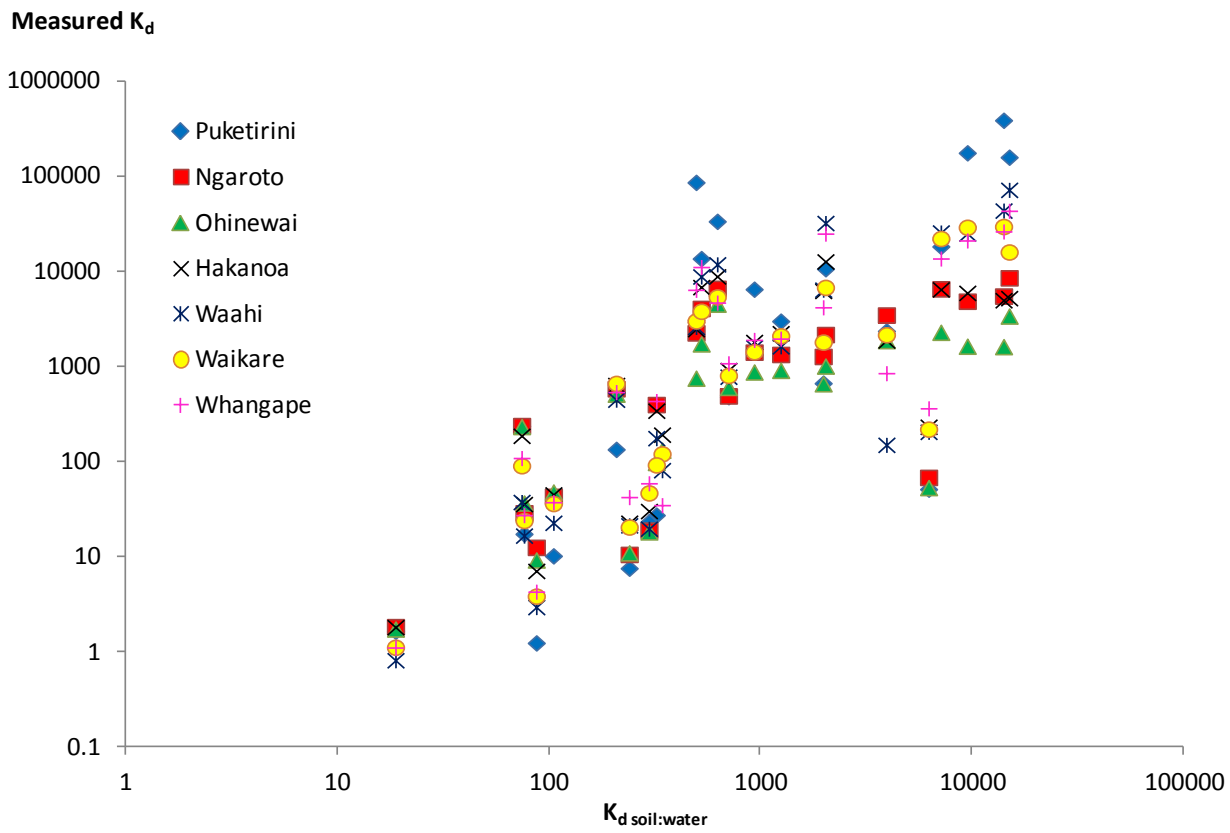

Figure 3.5. Relationship between measured K_d from sediment: water in 7 lakes and calculated K_d from soil:water for elements in Table 3.20.

3.4.4 Trace element concentrations in groundwaters of the Auckland, Taranaki, Waikato and Wellington regions, NZ

As, B, Cd, Cu, F, Sb and Zn were measured in groundwater bores as part of groundwater monitoring in the Waikato region (Hadfield 2013 and 2011). Summary data from autumn 2012 to the summer of 2012/2013 and for the corresponding period in 2010/2011 were collated (Table 3.21). As, B, Cu and Zn were sampled over both periods. There were very similar median concentrations for B and Cu for 2010/2011 and 2012/2013. However, median concentrations of As were about 20% higher in 2012/2013 compared to 2010/2011, which may be attributed to increased geothermal electricity generation. Geothermal generation contributes about ½ the load of As in the Waikato River (Kim 2010).

The element showing the greatest increase in median concentration for 2012/2013 compared to 2010/2011 was Zn, which had increased about 17 times its 2010/2011 value. There are multiple sources of Zn in the agricultural environment of the Waikato river catchment and the resulting compartmentalising of Zn is included in the discussion section below (Section 4.1.4.3).

Table 3.21. Summary statistics for selected trace element concentrations in 111 bores in the Waikato from Hadfield (2013, 2011).

Element	2012-13 Median ($g\ m^{-3}$)	Std Dev	Number of samples below detection limit	2010-11 Median ($g\ m^{-3}$)	Std Dev	Number of samples below detection limit
As	0.006	0.062	75	0.005	0.02	80
B	0.017	0.111	2	0.015	0.110	5
Cd	n.s.			0.00003	0.0001	90
Cu	0.001	0.012	44	0.001	0.0010	36
F	n.s.			0.025	0.070	77
Sb	0.001	0.005	97	n.s.		
Zn	0.009	0.542	10	0.005	0.160	10

n.s = not sampled that year

Summary data from the groundwater monitoring programme of the Auckland, Taranaki and Greater Wellington regions are compared with data from the Waikato region (Table 3.22). Most determinants in common showed similar levels present in groundwaters of the two regions. However, F was noticeably higher in groundwaters of the Taranaki and Wellington region, while Zn and SO_4 were higher in the Auckland region.

Table 3.22. Median values for selected trace element and other determinant concentrations from bores in the Auckland, Taranaki, Greater Wellington and Waikato regions.

Determinant (g/m3)	Waikato 2010-11 (111 bores) Median	Auckland 1998-2005 (24 bores) Median	Taranaki 1999-2007 Median	Wellington 1993-2013 Median
TOC	-	-	-	2.0
As	0.006	<0.001	-	0.005
B	0.017	0.09	-	0.026
Cd	0.00003*	-	-	0.00006*
Cu	0.001	0.002	-	0.001
Pb	-	<0.0001	-	0.0003
Zn	0.010	0.021	-	0.007
DRP	-	0.07	-	0.022
P	-	0.07	-	0.0255
F	0.03*	0.09	0.13	0.11
SO4	7.8	24.0	11.1	9.5
HCO3	-	-	-	57.0
Br	-	-	-	0.110
Cl	15.3	17	-	18.4

* = >50% of non-detects
- = not determined

Only 30% of the Waikato samples were above the detection limit for F of 0.05 g m^{-3} and averaged 0.053 g m^{-3}. In comparison, F was almost always above the detection limit in the Wellington samples. Levels of F in groundwater from both regions were well below drinking water guidelines (1.5 g m^{-3}) and levels likely to affect aquatic organisms (0.5 g m^{-3}), so were not considered of concern (Hadfield 2011, Camargo 2003). Concentrations of F varied less than other elements, suggesting less influence by external factors, such as land use. As F in

groundwater usually reflects the levels present in the surrounding lithosphere (Jha et al. 2011a), these results most likely reflect the natural level of F in groundwater.

Cd in groundwater bores in the Waikato region was monitored in 2010 due to interest in its accumulation in soil and the likelihood of leaching (Hadfield 2011). Cd was detected only in 15% of the samples but these samples tend to be from high intensity farming areas. There was a similar result for Cd in the Wellington region. The low number of detects inhibits confidence in the significance of these results, but the highest Cd concentrations were still only 50% of the drinking water standard limit values (0.05 μg m^{-3}, MoH 2008) for NZ (Figure 3.6).

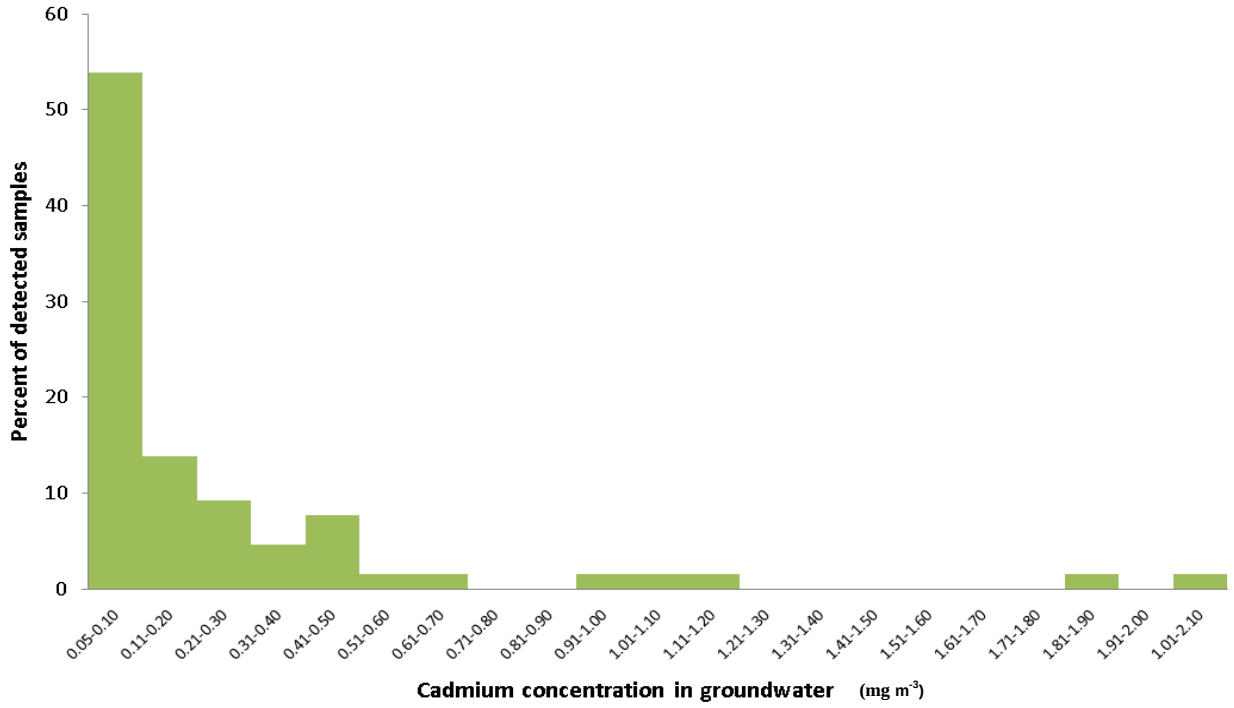

Figure 3.6: Frequency of Cd concentration in groundwater bores in the Waikato region, NZ. This graph relates only to the 15% of detected samples (those above 0.05 mg L^{-1}).

Hg was measured only in two groundwater samples in the Wellington region (Appendix 3.2). Results were below or at the detection limit; <0.00008 and 0.00008 g m^{-3}.

4. Discussion

4.1 Comparison with field data

4.1.1 Comparing the results of the ranking model against field data

Natural processes include weathering, leaching, plant uptake and reabsorption result in natural background concentrations of trace elements (e.g. Figure 3.1 for soil). Addition of fertilisers is purposeful act to change the background level of nutrients to increase production. On the other hand, both mineral and organic fertilisers were found to contain appreciable amounts of trace elements in excess of background levels (Table 3.2). The quantitative priority ranking model provides a ranking list of those element–fertiliser combinations with possible impact to the environment and health (Table 3.4), which may be useful in RMA section 32 analysis. One unexpected result from the quantitative ranking model is the high ranking of several elements such as B that are not normally considered priority trace elements in NZ.

Particularising into the factors underpinning the ranking model allows predictions that can be tested against the field data for soils (Table 3.7), fresh surface (Table 3.10) and ground waters (Table 3.21), lake sediments and estuarine sediments (Table 3.15). The implications of these results are discussed in the context of world literature for each element that was identified as having a possible impact on the environment and health.

4.1.2 Fluoride

The 5 mineral P fertiliser types were ranked 1-5 for F by the priority ranking model (Table 3.4) due to the high concentrations found in such fertilisers and the high likelihood of F accumulation (Section 3.2). Note there was no data on F in the organic fertilisers of this study. Although the accumulation of F in NZ soils is identified in the works of Loganathan et al. (2001, 2008) and Kim et al. (2008, 2014), it is not normally considered a priority trace element for human or environmental health in NZ, so it's top ranking was surprising. Consistent with the earlier work, F had very high concentrations in fertilisers derived from P rock (typically 1-4%, Table 2.2, Taylor et al. 2014c, Hedley et al. 2007) compared to natural levels in the environment (BG soils 269 mg kg^{-1}). These levels could be attributed to F being a component of apatite $Ca_5[PO_4]_3(Cl,F,OH)$. It also substitutes for isoelectric OH^- in soil

minerals, such as muscovite, amphiboles and micas, as both F^- and OH^- have similar ionic radii (Salminen et al. 2005).

Accumulation in soil is favoured as free F exists in soil and water as the anion (F^-), the most electronegative element in the periodic table (3.98 on the Pauling Electronegativity Scale). The higher the electronegativity of an element, the greater its attraction for bonding electrons (Pauling 1932). Al and Fe oxyhydroxides provide adsorption sites for F in soils (Delmelle et al. 2003, Omueti & Jones 1977) and Al oxyhydroxides are common weathering products in the soils studied here. The mechanism is reported as the adsorption of hydrogen ions to protonate Al-bound surface-active hydroxyl sites in the superficial layers of the mineral and induces F binding (Du et al. 2011).

The importance of amorphous Al oxyhydroxides in retaining F can be illustrated by comparing the results of this work with those of Davison & Weinstein (2006). Their research showed background soil concentrations of F to range between 20 and 750 mg kg^{-1}, with the higher concentrations generally found in clay soils. Conversely, this work showed natural background in sandy volcanic soils of the Waikato region of NZ, containing amorphous Al oxyhydroxides weathering products, had higher F (230-310 mg kg^{-1}) than natural background in clay soils derived from reworked sediments (Figure 4.1). These clay soils had very low total F (70-175 mg kg^{-1}) compared to studies of clay soils (250-750 mg kg^{-1}) presented in Davison and Weinstein (2006).

Another reason for F accumulation in soil is some fluoroapatite (the most common phosphate rock mineral) is likely to be unreacted in the fertiliser. Thus, it is likely that fertiliser applied F accumulates in soils as sparingly soluble CaF_2 and fluoroapatites or is adsorbed to hydrous oxides of Al (Ando & Hamada 1994, Omueti & Jones 1977).

As predicted, total F significantly accumulated in soils under kiwifruit, vegetable production, other horticulture and pastoral land uses (Table 3.6). The exception was for 2 soils under vineyards, which were not significantly different but were clearly elevated in F. Results were

consistent with previously reported accumulation of F in NZ soils, with PCA of the soils set showing F to be associated with P Cd and U (Kim et al. 2008, Loganathan et al. 2001).

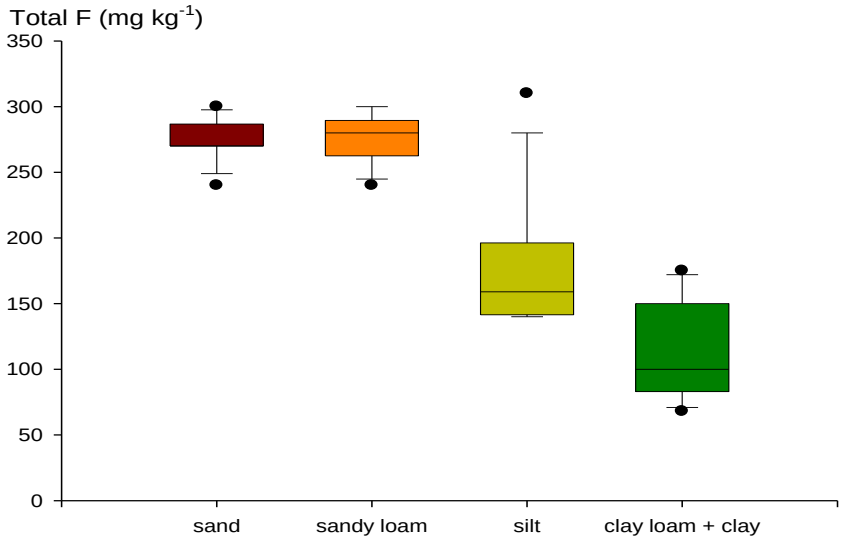

Figure 4.1: F content of natural background soils of different textures in the Waikato Region, New Zealand. Sand (>70% of particles > 0.1 mm), sandy loam (40-70% particles > 0.1 mm) silt (>40% particles 0.002-0.05 mm), clay loam + clay (>60% particles <0.002 mm)

Historically, the use of F-containing fertilisers derived from P rock has accounted for over 95% of the F in pastoral soils with the historic annual accumulation rate of F in Waikato soils estimated to have averaged 2.6 mg F kg^{-1} y^{-1} (Kim et al. 2008). Similarly, Cronin et al. (2000) estimated that F accumulation in surface (0-7.5 cm) soils from SP was 7.6 mg kg^{-1} y^{-1} in Allophanic soils under dairy and 4.2 mg kg^{-1} y^{-1} in Brown soils under meat production. Adjusted to a depth of 0-10 cm, to match the data of Kim et al. (2008) and this thesis, these equate to 5.7 and 3.2 mg kg^{-1} y^{-1}, respectively. The measured accumulation for F was 225 mg kg^{-1} (Table 3.8) and the estimated time fertiliser had been applied is 65 y. This gave an accumulation rate of 3.4 mg kg^{-1} y^{-1}, consistent with the previous studies. However, while Kim et al. (2008) only used data from the Waikato region, this study included samples from a wider geographic area. It also includes a wider range of soil types than Cronin et al. (2000). Thus, the average F accumulation appears consistent in many regions of NZ.

The overall estimated application of F as SP was 406 mg kg^{-1}, considerably more than the measured accumulation of 225 mg kg^{-1} in the top 10 cm of soil. However, all arable and most

pasture soils are ploughed, which would mix surface applied F deeper. Rabbits, earthworms and other soil organisms can also mix soil. Potential loss pathways also include leaching to groundwater, transfer in erosion sediments or dusts and volatilisation, e.g. as SiF_4, and removal in livestock.

Whether this applied F accumulates or not depends on the amount of F applied and soil pH as well as soil sorption sites. Poulsen (2011) showed that F retention mechanisms in the soil could be saturated and the proportion of soluble F increased as the soil total F concentration increased. A proportion of the total F is soluble and may leach through the soil into groundwater but the proportion often depends on soil and water conditions. The solubility and chemical speciation of F change with pH (Davison & Weinstein, 2006). While the slightly acid soils of New Zealand may adsorb almost all F applied, so removal by plant uptake or leaching is minimal, alkaline soils retain less F as repulsion by the negatively charged surfaces increased F solubility above pH 6.5 (Wenzel & Blum, 1992, Fluhler et al. 1982). At the other end of the pH range, F forms soluble complexes with Al (Loganathan et al. 2008, US Department of Health and Human Services 2003) and may be soluble at pH <4.9 if soils are highly organic (Loganathan et al. 2006). These complexes can also act as phosphate analogues in a variety of enzymes; Poulsen (2011) reported that soil F reduced phosphatase activity. Changes in land management, especially if pH is affected, could result in the mobilisation of accumulated F. That endemic fluorosis affects animals and humans in many countries including parts of India, Pakistan, Australia and Africa, is well known (Jha et al. 2011a, Lottermoser & Cleverly 2007, Underwood 1981). The load of F in diet reflects the intake in ingested food and water and (for grazing animals) ingested soil, which may be influenced by anthropogenic F. For example, while high F concentrations in groundwater may be due to natural F deposits, such as phosphate rock, agricultural applications of F were found to have enriched groundwater samples in the Murshidabad district of West Bengal, India, above 1 mg F L^{-1} and pose a potential threat of fluorosis (Kundu et al. 2009). In another study, the toxicological risk from F exposure due to ingestion of vegetables and cereal crops in Unnao district, Uttar Pradesh, India was assessed by Jha et al. (2011b) who found children of age group 3–14 years in the area were found to be at risk of fluorosis.

It should be noted that F enrichments estimated here are necessarily based on total F concentrations, rather than the acid recoverable fraction often used for other trace elements. Estimated values presented here may therefore represent minimum enrichments of any corresponding bioavailable fraction.

F accumulation in agricultural soils is a relatively new phenomenon in NZ, from the second half of the 20th century with the widespread adoption of topdressing of P fertilisers. Since P-fertilisers are applied to productive soils worldwide, it is reasonable to assume that similar magnitudes of anthropogenic F has been applied to agricultural soils across the globe (Stacey et al. 2010). If rapid accumulation of F occurs in soils, the range of possible adverse near-future effects broadens, and brings with it a greater chance that serious problems may emerge. As a proportion of its background concentration (269 mg kg^{-1}), agricultural soils (median 426 mg kg^{-1}) accumulated F at about 10% per decade from 1953-2013. F accumulation in agricultural soils should therefore be considered comparatively rapid.

That the vast majority of F is accumulating in soil is confirmed by the groundwater, freshwater lake sediment and estuarine sediment results (Tables 3.15, 3.21-22), which are near or below background concentrations and show no association between P fertiliser use or between total F and other fertiliser-derived elements. F was measured in groundwater in the Auckland, Wellington, Waikato and Taranaki regions, but concentrations were well below the drinking water guideline of 1.5 g m^{-3} (MFE 2013) (Table 3.22). The most comprehensive groundwater data for F was from the Wellington region. Over 3870 samples were analysed 1993-2013. Only 30% of the Waikato samples from 111 bores were above the detection limit (0.05 g m^{3}). The 24 bores monitoring in the Auckland region had a median F concentration of 0.09. Five bores were monitored in the Taranaki region, NZ from 1999-2007 with averages for each bore ranging from 0.03-0.30 g m^{-3} (TRC 2008). The results presented in Table 3.22 suggest little soil F is migrating into NZ groundwater and is in agreement with Loganathan et al. (2007) who found 21 years of annual application of mineral P fertiliser resulted in accumulation in the top 150 mm of soil but no change in F concentrations were detected below 180 mm. If a soil depth of 180 mm is mixed evenly with the same total application of F used in Table 3.8, the resulting soil accumulation should be 225.7 mg kg^{-1}, which matches the

measured accumulation of 225 mg kg^{-1}. Thus, it appears that bioturbation and ploughing mix F to about 180 mm.

Environmental effects from F accumulation in soils include toxicity, alterations to soil chemistry and function, and wider cross-compartment contamination. Toxicity concerns include those to soil organisms and terrestrial wildlife (Pascoe et al. 2014), phytotoxicity (Arnesen, 1997; Manoharan et al. 2007; Stevens et al., 1997), chronic fluorosis in grazing animals (Loganathan et al. 2001; Loganathan et al. 2008; Stacey et al. 2010), and potential for aluminofluoride complexes to interfere with biochemical signalling pathways. AlF_x complexes are of toxicological interest because they act as phosphate analogues in a variety of enzymes (Strunecka et al. 2012, Facanha & Okorokova-Facanha 2002). Alterations of soil chemistry and function include reduced turnover of SOM (Rao and Pal, 1978) and phosphatase activity (Poulsen, 2011), accelerated aluminosilicate weathering (Egli et al. 2001; Taylor et al. 2012), induced formation of AlF_x complexes in pore-water (Manoharan et al 1996), and altered uptake of F, Al, AlF_x and other F-complexed elements in crops and animals (Barbier et al. 2010; Stevens et al. 1997). Wider environmental impacts include potential for contamination of ground-water (Loganathan et al. 2006), toxicity to aquatic ecosystems (Camargo 2003), and perturbation of the atmospheric F cycle from fluorinated gases released from fertilised soils or during fertiliser manufacture (Mizane and Lassis, 2012). Volatile F-containing species are effective greenhouse gases (Brown et al. 2014).

Even though F is now thought of as an essential element in animals (Salminen et al. 2005), including humans, excessive levels result in fluorosis, and F is considered one of the most significant groundwater contaminants in some countries (Jha et al. 2011a). Although there may be potential human health effects, the main health impact of excessive F in NZ is seen in animal welfare. The F content of superphosphate is in the region of 10,000 – 40,000 mg kg^{-1}, with a typical NZ estimate being about 15,000 mg kg^{-1}. At this concentration, ingestion of superphosphate by grazing stock would be sufficient to cause fluorosis. Death of free-range stock grazing pasture after fertiliser addition is reasonably common (e.g. 3-4 animals per year in the Waikato, Ross Vowles, Glenview Vets), and euphemistically called phosphate poisoning (O'Hara et al. 1982). During the period 1965-75, a total of 37 poisoning outbreaks

were reported in NZ by the Ruakura Animal Health Laboratory. Frequently, fertiliser had been applied to pasture carrying frost or dew that dried on the foliage in the absence of rain (Edmeades 2004).

Nevertheless, the accumulation of F in soil is likely to increase uptake of F in all stock, not just those exposed directly to phosphate fertiliser, as plant uptake of F increases, and as ingestion of soil is the major source of dietary F (93% of dietary F, Grace et al. 2005). Cronin et al. (2000) estimated that for sheep, the tolerance limit for dietary F should be reached at soil F concentrations ranging from 372 to 1461 mg kg^{-1}, while for cattle the range was 326 to 1085 mg kg^{-1}. In comparison, the range of F concentrations found in this study ranged from 68-900 mg kg^{-1}. However, the potential risk of chronic fluorosis occurring in animals grazing pastures in NZ is usually low (Grace et al. 2008) as long as there is sufficient pasture cover. A reason for this is the proportion of F that is soluble is much lower in NZ agricultural soils than the proportion reported in the literature as these sites had been contaminated with F from industry (Loganathan et al. 2006). However, the increase in periods and length of drought caused by climate change and excessive grazing of pasture from increased intensification are likely to inflate this risk. Lactating cattle are particularly sensitive to F due to their negative calcium balance (Loganathan et al. 2006).

Higher soil F concentrations in soil increase the risk of toxicity to terrestrial wildlife species (Ranjan and Ranjan, 2015). Pascoe et al (2014) derived Risk Based Concentrations for [F] in soil for an area contaminated by phosphate ore processing facilities in southeastern Idaho for four wildlife species. Lowest Observed Adverse Effects Levels ranged from 659 mg kg^{-1} (deer mouse) to 2537 mg kg^{-1} mg kg^{-1} (red-tailed hawk). In the present work 5% of soils exceeded 650 mg kg^{-1} (Appendix 1.2) suggesting that onset of F toxicity may now be starting to be realised in some small mammalian species after about 60 years of accumulation, depending on species sensitivity, ecological niche and F soil bioavailability.

Poulsen (2011) reported leaching experiments where phosphatase activity was significantly reduced due to F's ability to forms strong complexes with Al that mimic phosphate groups. This work also showed that F retention mechanisms in the soil could be saturated and the

proportion of soluble F increased as the soil total F concentration increased. As AlF_x can act as phosphate analogues in a variety of enzymes, they are able to influence an array of biological pathways. It follows that F can have great influence on both animals and microbial wellbeing.

While ingestion of soil containing high concentrations of F may lead to chronic fluorosis in stock, a similar situation could occur for young children playing in soil on the farm or with phosphate fertiliser. There appears a lack of risk-based guidelines for soil F. This work is needed to direct research on the management of the impacts of F to animals and ecosystem receptors.

Some plants are sensitive to soil F concentrations (Figure 4.2), while others can tolerate higher concentrations. A high internal F concentration disturbs almost all the physiological and biochemical process in plants (Baunthiyal et al. 2014), with notable effects on germination, photosynthesis, respiration, cellular enzyme activity, cell signalling, gene expression, reproduction, growth and yield (Panda 2015). F can also have indirect effects on plants such as inhibiting P uptake (Facanha & Okorokova-Facanha 2002).

Figure 4.2: Fluoride Toxicity in Spider Plants. (Rosie Lerner, Purdue University)

Stevens et al. (1997) reported general symptoms of F toxicity including growth reductions accompanied by leaf tip chlorosis (yellowing) and necrosis (burning) for tomato grown in solutions of 10 µM F but oats were unaffected up to 1682 µM. Jha et al. (2009) reported visible symptoms of F toxicity (tip burning and death of the plant) in onions in soil with pH 8.4 and >500 mg F kg^{-1} soil while spinach showed no visible symptoms of F toxicity in the same soil with up to 670 mg F kg^{-1} (Jha et al. 2008). However, the F content of the spinach increased linearly and Jha et al. (2008) inferred spinach has a distinct mechanism of partitioning of water labile F and total F in the tissues.

Soil F concentrations determined in this work are commensurate with levels known to cause chronic toxicity and/or reduced yield in plants. Mishra et al. (2014) reported significant decreases in Net Primary Productivity for several crops as F concentrations increased from a natural baseline of 95 mg kg^{-1} to 158 mg kg^{-1}. Similarly, Telesiński et al. (2012) reported that 50% inhibition of root growth occurred at soil F concentrations of 441 mg kg^{-1} for white mustard and 503 mg kg^{-1} for spring wheat. A 500 mg F kg^{-1} soil guide was also suggested by Jha et al. (2008). In this study, 43% and 31% of all fertilised soils had soil F concentrations exceeding 450 mg kg^{-1} and 500 mg kg^{-1}, respectively (Appendix 1.2).

However, the amount of F taken up by plants in NZ appears to be unrelated to the total F concentration of the soil, and instead depends on soil type, pH, SOM, and Ca and P content (Cronin et al. 2000). Cronin et al. (2000) reported that several studies and their own data failed to show significant increase in foliar F content with increased soil F content, while Davison & Weinstein (2006) reported plants growing in the vicinity of a source of atmospheric F had foliar F concentrations dominated by direct uptake. Although the F concentrations in 31% of the NZ soils sampled were greater than the 500 mg F kg^{-1} soil guide suggested by Jha et al. (2008), plants appear currently unaffected due to the low solubility of F at the usual soil pH of 5.5-6.5. However, the average pH of natural background NZ soils is

5.0 and continual applications of lime are needed to keep soil pH at the optimum for pasture and most arable crops, which keeps soluble F levels negligible.

One crop that may be vulnerable to high F concentrations is tea. NZ is an exporter of high quality tea to China. Tea trees (*Camellia sinensis*) naturally take up large quantities of F (and Al) from acidic soil, which accumulates mainly in the tea leaves in the form of Al and F complexes (Yi & Cao 2008, Wong et al. 2003). Accumulation increases with leaf age. Yi & Cao (2008) reported a tea product, brick tea, which is fermented and pressed into brick-shape, had extremely high F concentrations (52.5–1175mg/kg), while tea made from black tea bags also had high F concentration (1.15–6.01 mg/l). Black tea bags and brick tea are made with low cost, and older tea leaves. F may also influence the Al content of tea as Al-F complexes contribute to total soluble Al and F in soil solution, particularly in acidic soils (Wong et al. 2003). McLachlan et al. (1996) pointed out that Alzheimer's disease is associated with the Al content in the human brain, therefore, the high Al content in tea may be a concern.

Most other plants do not readily take up F. Stevens et al. (2000) showed five plant species commonly found in improved pastures in Australia (and NZ) would not accumulate concentrations of F harmful to grazing animals through root uptake in neutral pH agricultural soils. The risks from F addition to soils in mineral P fertilisers leading to appreciable increase in F in food or the reduction in pasture growth or impacts on animal health on well managed farms were therefore low. Nevertheless, one source of F accumulation in the food chain may be deer antler anti-aging health supplements as F is sequestered in animal bone, teeth and horn, e.g. deer antlers and bones have been shown to have high F concentrations of about 2000 mg kg^{-1} in animals fed high F diets (Headley et al. 2007).

There may also be some benefits of adding F to soil, although this may depend on the type of fertiliser applied. Manoharan et al. (1996) reported soil solution F was increased by the addition of rock phosphate and superphosphate fertilisers but there was a corresponding decrease in toxic Al species. This was due primarily to complexation of Al with F derived from these fertilisers forming less-toxic Al-F complexes. In contrast, NH_4 containing phosphate fertilisers such as DAP decreased soil pH and increased the formation of more-

toxic Al species in the soil solution (Manoharan et al. 1996). However, continuing to add F to the soil may increase the concentration of Al-F complexes to toxic levels. Manoharan et al. (2007) added higher rates of F to strongly acidic soils and barley root growth was reduced due to the toxicity of Al-F complexes formed in soil solution.

There is little research on the impacts of F on the soil matrix but there are some indications that it can disrupt the Al minerals and cause soils to weather more quickly (Taylor & Kim 2009) such as breaking down Al and Fe oxides/hydroxides and solubilising SOM in the soil (Arnesen 1998). One effect of enhanced weathering appears to be the release of elements normally held within the mineral structure. These elements are normally strongly resistant even to attack by strong acids. One such element is U, which shows considerable increase in solubility with fertiliser addition. About a third of the acid soluble fraction appears to be from enhanced weathering and two thirds directly from U contaminated fertiliser addition (Taylor & Kim 2009, Kim et al. 2008).

No authors have yet considered the potential for F to induce toxicity to wildlife through enhanced Al mobilisation (Manoharan et al. 1996). However, Exley et al. (2015) advanced an hypothesis that the global decline in pollinator species may be linked to Al toxicity from contaminated pollen and nectar, providing evidence that bumblebee pupae from colonies placed in both urban and rural areas contained Al at concentrations that should be neurotoxic. If correct, the findings of this study may have special significance, because F-induced Al mobilisation (as the phosphate analogue AlF_x) would represent a suitably broad-scale mechanism by which plants, pollen and nectar may have been taking up progressively more Al from rural soils.

As F is not regularly measured in regional council surface water monitoring in NZ, there are data for F in only for the Waikato River from this study. The median value of 0.18 g m^3 compares well with the FOREGS geochemical atlas of Europe world average in stream water of 0.1 g m^3 (Salminen et al. 2005). Aquatic organisms may be at increased risk of adverse health effects if F levels in water increase. Freshwater species appear to be more sensitive to F toxicity than estuarine and marine animals as the bioavailability of F is reduced with

increasing water hardness. Camargo (2003) reported, for soft waters with low ionic content, an F concentration as low as 0.5 g m^3 can adversely affect invertebrates and fishes, especially net-spinning caddis fly larvae and upstream-migrating adult salmons.

F concentrations in lake sediments were similar to those for background soils but the median concentration for Appletree estuarine sediment was appreciably higher. A similar pattern was seen for Mg, while PCA of the lake sediments showed F and Mg to be positively loaded on component 2 (Table 3.16). In addition, the highest correlation for F using Spearman's rank correlation was with Mg (r = 0.51, Table 3.17). So, the Mg content appears to control the F content of carbonate sediment, possibly by coprecipitation of F and Mg with $CaCO_3$ (Ohde & Kitano 1980). However, the Appletree estuarine sediments are not carbonates so another mechanism must be involved but without further data it would be speculation to suggest one. F was not measured in the other estuarine sediments in this study.

Although F concentrations are clearly elevated in pastoral soils, sediments of lakes situated in pastoral catchments did not show noticeable excess F. These results suggest migration of F in NZ has been limited in proportion to the natural magnitude of F in bed sediments.

Since P fertilisers are applied to productive soils worldwide, it is possible that similar magnitudes of anthropogenic F enrichment have been occurring in P-treated agricultural soils across the globe (Stacey et al., 2010). Globally the proportion of added F retained by soil or leached will vary. While the slightly acid soils of New Zealand may adsorb almost all F applied so removal by plant uptake or leaching is minimal, alkaline soils retain less F as above pH 6.5, repulsion by the negatively charged surfaces increases F solubility (Wenzel and Blum, 1992; Flühler et al., 1982). Also, Poulsen (2011) showed that F retention mechanisms in soil could be saturated and soluble F increases in proportion to total soil F.

These results suggest a need for a systematic examination of ecotoxicity, altered Al chemistry and organic matter turnover, and increased uptake of F and F-complexed elements in crops, animals, and the human diet, and transport to other environmental compartments. On the other hand, groundwater and lake sediment data in this work showed no clear evidence for

substantial movement of anthropogenic F from soils to freshwater receiving environments under current conditions. However, F mobilisation may increase in future in the event of changes to land management which affect pH, changes to climate which increase rainfall intensity, or soil F saturation.

The F content of mineral fertilisers can be reduced considerably by simply not putting F removed by scrubbers during manufacture back into the fertiliser. Recovery of F compounds during fertiliser manufacture is theoretically and practically possible using existing technologies during the processing of raw phosphate (Górecki 1994), e.g. in acidic water, F can be removed by adding lime to pH 3 to precipitate most of the F as CaF_2 (Ando & Hamada 1994), so it may be possible for fertiliser manufacturers to reduce F further for liquid fertilisers or during the manufacturing process for granular fertilisers.

F can impact animal health, is known as a major contaminant of groundwater in some countries, and readily bioaccumulates in some plants like tea. Understanding of the environmental consequences of the continued application of F in mineral fertilisers is needed by policy makers to provide environmental protection and the sustainable production of agriculture, especially in the context of RMA section 32 analysis. Such work could identify and assess the risks to soil and aquatic organisms, to plants and to farm animals, and underpin a review of current soil guidelines.

4.1.3 Uranium

The priority ranking model ranked U from TSP, AP, RRP, SP and Blended mineral fertilisers 7^{th}, 9^{th}, 11^{th}, 14^{th} and 15^{th}, respectively, while U from piggery, poultry, cattle and fish products ranked much lower at 93^{rd}, 94^{th}, 153^{rd} and 192^{nd}, respectively (Table 3.4). U is another element not normally considered a priority trace element for human or environmental health, outside the nuclear industry, although the link with mineral P fertiliser is well established (Taylor 2007, 1997b, Rothbaum et al. 1979). Thus, guidelines to direct research on the management of the impacts of U to animals and ecosystem receptors have come about due to studies associated with the nuclear industry. The United States Nuclear Regulatory Commission has established a residual contamination criterion for natural U in soil of 10 pCi g^{-1},

equivalent to 30 mg kg^{-1} (USNRC 1992), while the Canadian Council of Ministers of the Environment (2007) gave the final Soil Quality Guidelines for U for the protection of both human and environmental health as 23 mg kg^{-1} soil for agricultural land use, 23 mg kg^{-1} for residential/parkland land use, 33 mg kg^{-1} for commercial land use and 300 mg kg^{-1} for industrial land use. The use of these guidelines and whether they include all hazards associated with the diffuse contamination of U derived from application of fertilisers is still being debated, e.g. U exhibits harmful effects not predicted by its radioactivity (Busby & Schnug 2008).

U is found in all rocks, soil and water and is present in all phosphate rock at various levels (Dupré de Boulois et al. 2008, Gavrilescu et al. 2009). Concentrations of U in sedimentary rocks relate to the redox conditions at the time of their formation, e.g. the highest concentrations of U are found in organic rich facies associated with phosphatic sediments formed in anoxic environments (Salminen et al. 2005). It has been proposed that the marine phosphorites of the Chatham Rise, New Zealand, be mined for P fertiliser as these have very low Cd concentrations of about 2 mg kg^{-1}. However, the U concentrations are very high and can exceed 500 mg kg^{-1} (Kolodny & Kaplan 1970), so using fertiliser made from this source would increase the rate of U accumulation.

At low concentrations U has beneficial effects, e.g. hormesis, on cancer mortality and mortality from all causes in populations exposed to low-dose radiation. Pollycove (2007) detailed this effect as improved DNA damage control, i.e. reduced persistent mis- or unrepaired DNA damage by reducing the number of mutations that accumulate during a lifetime. However, U is also chemically toxic causing skin, lung, intestinal and bone marrow disorders, particularly where individuals have been chronically exposed by skin contact, ingestion or inhalation of dust, such as in phosphate mines and processing (Canu et al. 2012, 2011, Raymond-Whish et al. 2007, Santos et al. 1995). In addition, U is a radioactive α emitter and exhibits genomic and other harmful effects not predicted by its radioactivity (Busby & Schnug 2008). An explanation for these anomalies is that the absorption of gamma and X-rays increases rapidly with atomic number of the adsorbing element (Busby & Schnug 2008). So, elements of high atomic number Z which also have a significant affinity for DNA,

such as U, will result in anomalously high absorption of natural background radiation by the DNA and its re-emission as photoelectrons. This represents a focusing of natural background radiation (and any other external gamma or X-rays) into the DNA (Busby & Schnug 2008).

High median U concentrations were found in all fertilisers derived from P rock compared to BG soils (typically 34-95 and 2.9 mg kg^{-1} respectively, Table 2.2, Taylor et al. 2014c), consistent with the author's MSc thesis and papers arising from it (Taylor 2007b, 1998, 1997, 1996), and international literature (Schnug and Haneklaus 2015, Smidt et al. 2011). Also, U was predicted to accumulate in the high K_d conditions found in NZ soils (USEPA & USDE 1999).

Levels in the organic fertilisers were below background soil values (Table 2.2). Also, the animals from which these organic fertilisers were derived are generally farmed for food, which is tested for harmful components, e.g. as part of the New Zealand Total Diet Study (MPI 2011). These animals appear to live healthy lives until they become meat. Overall, this outcome suggests fertiliser impurities ranked 93rd and above in Table 3.4 have minor impact on health and the environment

The mobility of U in soil is controlled by the formation of UO_2^{2+} (Salminen et al. 2005) and is highly immobile in high K_d conditions and extremely mobile in low K_d conditions, e.g. U is generally more mobile in oxidising, alkaline and carbonate rich environments. U impurities in phosphate fertilisers may accumulate in the soil (Rothbaum et al. 1979) where they can be taken up by plants and be transferred into the food chain, or, conversely, be leached into ground and surface water (Jones 1992). The oxidation state of U, the presence of SOM and pH are major controlling factors in U sorption, mobility and plant availability (Chabaux et al. 2003, Echevarria et al. 2001, Ebbs et al. 1998) with U found predominantly in soils in one of two states, U(VI) and U(IV). U(VI) dominates in oxidizing environments. It is strongly held to the soil at mildly acid pH but forms highly soluble carbonate complexes at alkaline pH and uranyl ions are mobilised at highly acid pH, while U sorption onto minerals is increased in the presence of SOM, which can act as an electron donor. Similarly, U is very strongly held on

peat soils (Sheppard et al. 1983). NZ soils are, generally, slightly acid (5.9) with high SOM (total C 5.8%, Appendix 1.2).

As predicted, U significantly accumulated in NZ soils under all the fertilised land uses assessed in this study (Tables 3.7-8), and very high concentrations of U and P, up to 10 times or more than concentrations in Table 3.7, were found in soil next to fertiliser storage areas (Taylor & Kim 2008). The strong relationship ($p<0.0001$) between U and P demonstrated the connection between mineral P fertiliser and U, consistent with previous studies in NZ (Schipper et al. 2011, Taylor 2007, 1997b, Rothbaum et al. 1979).

The overall estimated application of total U as SP was 1.33 mg kg^{-1}, somewhat less than the measured accumulation of 1.80 mg kg^{-1} in the top 10 cm of soil (Table 3.8). Like for F, mixing by ploughing and soil organisms would apply, so the estimated value should be greater. However, it is more than the acid recoverable value of 0.76 mg kg^{-1}. Taylor & Kim (2008) showed U added to soil in fertiliser was extracted by acid although U relocated from the more available to the more resistant fractions of the soil over time. Thus, the increase in acid recoverable U should match the increase in total U. As there is no other known source of U to NZ soils, the difference may be due to the errors in measuring low concentrations of U by XRF.

Nevertheless, the accumulation rates for total and acid recoverable U were estimated from the data in this thesis by dividing the difference between BG soil and the median concentration of all fertilised sites from Table 3.8 by the estimated time fertiliser had been applied (65 y). This gave accumulation rates of 0.027 and 0.011 mg kg^{-1} y^{-1} for total and acid recoverable U, which appears consistent with previous studies in NZ, 0.033 ± 0.008 mg kg^{-1} y^{-1} (Taylor 2007b), and overseas, 0.004 mg kg^{-1} y^{-1} with a range of 0.001-0.015 mg kg^{-1} y^{-1} (Rogasik et al. 2008), 0.009 mg kg^{-1} y^{-1} (Takeda et al. 2006), and 0.015 mg kg^{-1} y^{-1} (Tunney et al. 2009).

NZ's soils high SOM content, high sorption capacity and slight acidity clearly lead to the accumulation of U. The redistribution of applied U from the more available to the more resistant fractions of the soil recorded by Taylor & Kim (2008) can be attributed to the

predominance in NZ of well oxidised, mildly acidic, highly organic soils, which have a strong affinity for U sorption. Very little U is soluble under these soil conditions with < 1% of the acid soluble fraction in soil solution (Taylor & Kim 2008).

While total U is increasing due to mineral P fertiliser additions, fertiliser additions have also been reported to enhance weathering, which increases the availability of native, recalcitrant U through enhanced weathering of soil minerals (Taylor et al. 2012, 2010, Taylor & Kim 2009). About a third of the acid soluble fraction appeared to be from enhanced weathering and two thirds directly from U contaminated fertiliser addition (Taylor & Kim 2009, Kim et al. 2008). So, about 0.5 mg kg^{-1} of the acid recoverable U of 0.76 mg kg^{-1} would be attributed to fertiliser applied U.

As well as the contribution from enhanced weathering, the higher accumulation rate estimated in this study may reflect intensification of farming with increased P fertiliser application. Applications of P of >40 kg ha^{-1} y^{-1} are commonly recorded for dairy and annual cropping soil quality monitoring sites in the Waikato region, with several sites recorded receiving about 90 kg ha^{-1} y^{-1} (Appendix 1.2). An interview with one of the longest established and largest vegetable growing companies revelled applications of fertiliser 40 years or more ago were up to 3.5 t ha^{-1} although P content was not known exactly (Simon Wilcox, A S Wilcox & Sons Limited). This not only increases U content directly by adding U but may also increase the enhanced weathering effect.

Another possible contributor is the U content of past and present fertilisers. In the past, mineral P fertiliser was derived from the ancient guano deposits mined from Ocean Island, Nauru (64 - 121 mg U kg^{-1}, Williams 1974, Syers et al. 1986) and Christmas Island (31 - 56 mg U kg^{-1}, Trueman 1965). Current U concentrations in fertilisers depend on the source of P rock imported into the country and this is bought on the open world market. There is no regulation of the U content in P rock imported into NZ. The amount of U in current fertilisers may be greater than the assumed value used in calculating the estimated application.

There is very little other research on U behaviour in NZ soils and the discussion below is dominated by the international literature. Accumulation of U from phosphate fertiliser is a worldwide phenomenon and has also been reported in Germany (Utermann & Fuchs 2008, Rogasik et al. 2008), England (Rothbaum et al. 1979), Japan (Yamaguchi et al. 2009, Takeda et al. 2006), Australia (Lottermosser 2009), Canada (Sheppard et al. 2009b), USA (Zielinsky et al. 2006) and Ireland (Tunney et al. 2009). However, U can be mobile depending on soil conditions, and significant U concentrations can appear in deep soil horizons, in groundwater, and in the sea, e.g. impurities from mineral P fertiliser application were identified as a source of increased U in the Baltic Sea (Skwarzec et al. 2010) and anomalies in the U: Cl ratio were most likely caused by high U concentrations in inflowing streams (Åström et al. 2009). Similarly, high U concentrations in surface water and shallow groundwater have been attributed to mineral P fertiliser application in Canada, Germany and Croatia (Weir 2004, Smidt et al. 2012, Barišić et al. 1992).

Importantly, the soil environment is not constant and changes in the environment affect the mobility of U. Thus, historic accumulation in soil does not guarantee U will stay immobile. Increases in the greenhouse gas CO_2 may lead to an increase in CO_2 pressure in soil solutions, which reduces U (VI) adsorption by promoting the formation of carbonate complexes. Accelerated weathering of aluminosilicates may result in the release of elements normally held within the soil mineral matrix, including U (Taylor et al. 2012, Taylor & Kim 2009). Increases in the ionic strength of soil solution increases competition for exchange sites, which may force U(VI) from soil exchange sites into soil solution. Thus, U(VI) can be particularly mobile in high ionic-strength solutions (USEPA & USDE 1999, Taylor 1997b). Conversely, U may be mobilised if there is very little in soil solution, e.g. Crancon et al. (2010) observed increased U mobility after a drop of solution ionic strength in the field after a rainfall event.

Adding to the complexity of U sorption/desorption behaviour in the field, these environmental factors may interact with each other, e.g. U uptake by wheat and tomato depended upon the U concentration in the soil and the amount of irrigation applied (Gulati et al. 1980).

Interactions with other elements and compounds also effect U adsorption although these interactions have been shown to be complex (Chabaux et al. 2003), e.g. the presence of the alkaline earth elements Ca, Mg and Sr have been shown to decrease U adsorption between pH 6.5 and 9 (Nair & Merkel 2011). This reduction in adsorption was attributed to the formation of zero valent and anionic complexes of alkaline earth uranyl carbonate species. Similarly, carbonate in solution inhibits U sorption onto minerals (Bednar et al. 2007). However, U(IV) can also form strong complexes with dissolved organic matter (DOC), increasing its solubility, e.g. humic acid generally decreases U sorption to soils by partitioning into the organic phase (Bednar et al. 2007, USEPA & USDE 1999).

In contrast, U(IV) dominates in reducing environments where it tends to hydrolyse and form strong hydrolytic complexes or sparingly soluble precipitates. Several soil organisms can also reduce U(VI) to U(IV) and this natural process has been used in the leaching of U from mine tailings. Yamaguchi et al. (2009) found most of the phosphate fertiliser-derived U was either incorporated into the SOM or poorly crystalline Fe/Al minerals in the surface soil of agricultural fields, depending on soil redox conditions. SOM was an important pool of U in oxidised upland field and pasture soils, whereas poorly crystalline Fe/Al minerals were important pools of U in paddy soil experiencing alternating redox conditions. Similarly, periodic changes in redox potential from wetting and drying cycles in some NZ soils resulted in co-precipitation of U with Mn in ironpans and concretions ($r = 0.78$, $p<0.001$, Appendix 4.1).

Although U is accumulating in fertilised NZ soils, concentrations were close to or below their detection limits in lake and river waters (Table 3.10). Median values ranged from 0.00001-0.00005 gm^{-3}. In comparison, the FOREGS geochemical atlas of Europe reported 0.32 $\mu g\ l^{-1}$ as the median for 807 water samples, so the levels of U in NZ surface fresh waters appears low in general (Salminen et al. 2005).

It was observed that one lake, Lake Waahi, had particularly higher U concentrations in the water column at times compared to those of other lakes. B, Mo, V, pH as well as chlorophyll, phycocyanin and turbidity could be elevated when U levels were higher (Table 3.11), and the

high U concentrations were attributed to water pH change to >8.5 due to algal blooms. This phenomenon also occurred on two other lakes during algae blooms, but the increase of U in the water column was smaller than the increase at Lake Waahi.

Average acid recoverable U concentrations in sediments were similar for all three lake types, the Appletree, southern Firth of Thames estuary, and background soil (Table 3.15). U was lower, on average, in West coast and northern Firth of Thames sediments, but this was not significant. The median acid recoverable U concentrations for all sediment samples, NZ background soils (rather than the world median total U of Table 2.2) and NZ fertilised samples were 0.87, 0.69 and 0.85 mg kg^{-1} respectively (Tables 3.8, 3.15 Appendix 1.2). Despite the increase in U concentrations in fertilised soils, sediment concentrations have remained close to those of background soil, so there is little evidence of transfer of U to lake and estuarine sediments. Also of note is that Lake Waahi shows similar U concentrations in sediments to concentrations found in other lakes despite at times having elevated U water concentrations a times (Appendix 3.1). Patterns of U in stream water in Europe tended to be virtually the opposite to patterns in stream sediment (Salminen et al. 2005) and this seems to be the case here as well.

PCA analysis showed lake sediment U was associated with Mn and K (Tables 3.16). Regression analysis using Spearman's Rank Correlation showed the strongest correlation with U was with K ($r = 0.66$). Similar results were obtained for stream and floodplain sediments in Europe (Salminen et al. 2005). The crustal K:U ratio is within an order of magnitude of 1×10^4 for a wide range of rock types (Wasserburg et al. 1964, Heier & Rogers 1963, Murray & Adams 1958). So, the existence of a natural relationship between K and U in sediment is possible. However, an exception is phosphate rock. The K:U ratio of the phosphate rock in the fertiliser study (Section 3.1.2) had a median K:U ratio of 16 (Table 4.1, Appendix 2.3). Rock sourced from Egypt (K:U ratio 1749) had a much higher ratio than rock sourced from other areas.

Table 4.1. K:U ratios of rocks soils and sediments from literature and measured in this study

Material	K:U ratio	Source
Oceanic tholeiitic basalt	~14000	Tatsumoto et al. 1965
Basalts	16700	Heier & Rogers 1963
Igneous rock	~10000	Wasserburg et al. 1964
Sands and sandstones	14200	Murray & Adams 1958
Soils from Cyprus	2800	Tzortzis & Tsertos 2004

Measured K:U ratios				
Material	Average	Median	Minimum	Maximum
Phosphate Rock	107	16	3	1749
Lake sediments	844	805	458	1766
Estuarine sediments	3280	2945	1081	6364
Background soil	1059	971	191	3571
Fertilised soil	476	379	86	2839

The K:U ratios of soils and the lake sediments were much lower than the ratios usually reported in rocks (Table 4.1). The higher soil K:U ratios were found in nonfertilised soils, while the lowest ratios were associated with high P, Cd, F and U values suggesting a direct connection with mineral P fertiliser additions. Both U and K undergo weathering processes that can enhance U relative to K as rock is turned into soil (Wilford et al 2009). However, the addition of very low K:U ratio mineral P fertilisers tends to lower the soil K:U ratio further. The K:U ratio may be useful in identifying historic fertiliser additions.

Patterns of U in stream water in Europe tended to be virtually the opposite of patterns in stream sediment (Salminen et al. 2005). Consistent with Salminen et al. (2005), U was not associated with K in surface waters.

There are a wide range of organisms living on and in NZ soils, waters and sediments. Both terrestrial and aquatic organisms are reported to take up U. Plants (Dushenkov 2003, Ebbs et al. 1998), bacteria, (Sar et al.2004), algae (Kalin et al. 2005), and fungi (Dupré de Boulois et al. 2008, Baeza & Guillén 2006) were shown to accumulate U. The biological activity of

these organisms can affect U speciation and thus bioavailability by modifying the pH, extracellular binding, transformation and formation of complexes or precipitates, possibly enhancing U entry into the food chain.

However, the NZ environment does not favour U entry into the food chain due to soil conditions. Root U concentrations have been shown to have a distinct U-shaped regression line with solution pH, with a minimum at pH 6.5 (Tyler and Olsson 2001). The average pH (about 5) for Waikato soils is 5.8 with higher pH (6-7) for most horticultural and cropping soils and lower pH for native bush and production forestry.

In contrast, the free uranyl ion, U phosphate and U carbonate complexes are available forms of U under alkaline pH conditions (Vandenhove et al. 2007, Laroche et al. 2005, Ebbs et al. 1998). Based on the example of Lake Waahi, U may be solubilised from sediment during the alkaline water conditions during algae blooms. It is not known if this U is taken up by aquatic plants or fish once oxic conditions return, and consideration could be given to further investigating this phenomenon.

Another impact of U in soils is the natural radioactive decay to form daughter products such as highly radioactive radon gas (U→Ra→Rn, Taylor 1997b), which are of greater concern to environmental and human health than U itself. Soils and rocks, such as phosphate rock, that contain high levels of U also store natural deposits of Rn. Rn (half-life of 3.8 days) is continually being formed in soil and released to air as a result of the extended half-lives of U (half-life of 4.51 $*10^9$ y) and Ra (half-life of 1620 y), and their abundance in the earth's surface. Atmospheric Rn is not considered an issue of health concern because it is rapidly diluted to low levels by circulation throughout outdoor air. However, Rn can be an issue in confined spaces, such as house basements, caves (Kim & Taylor 2013) and potentially in enclosed fertiliser storage facilities.

NZ should consider establishing a risk-based soil guideline value for U to direct research on the management of the impacts of U to animals and ecosystem receptors. Until such a guideline is derived, a conservative approach in land management is suggested because of the

chemical and radiotoxicity of U (International Labour Office 1972) and our lack of knowledge of safe levels in soil. Until risks have been better characterised, it may be safest to treat soil that is excavated from these areas as hazardous waste.

4.1.4 The M^{2+} cations

4.1.4.1 Commonalities of the M^{2+} cations

Some elements have similar chemical properties, exhibit similar behaviour in soil, and can be considered together. Many of the common contaminants in fertilisers are cationic in nature, e.g. Cd, Cu, Pb, Ni, Zn etc. are all divalent cations as the predominant charge on them is 2^+ and these can be collectively called the M^{2+} cations. This group of M^{2+} cations is discussed together and then individual elements are discussed.

The range of factors which influence the bioavailability of M^{2+} cations in soils means that the total level in soil does not necessarily correlate well with the plant-available fraction nor with the risk of leaching to groundwater, e. g. not all M^{2+} cations in the soil will be in a form that is available to plants (BRS 1997). Because of this complexity, uncertainty remains regarding the relationship between the levels of M^{2+} cations in soil, the expected levels of M^{2+} cations in food grown on the same soil and the anticipated levels in groundwater.

After the total metal concentration, the major factor affecting the mobility and bioavailability of M^{2+}cations in soils is determined primarily by soil pH, e.g. in acidic soils, proportionately more Cd is released to the soil pore-water, therefore making it more available to plants, while in strongly alkaline soils, Cd is more strongly fixed by the solid phases and becomes relatively unavailable (BRS 1997). Kabata-Pendias and Pendias (2001) note that, “in nearly all publications on the subject, soil pH is listed as the major soil factor controlling both total and relative uptake of cadmium”. Protons directly compete with M^{2+}cations for surface adsorption sites (on clay minerals, organic matter, and Fe and Mn oxides), and also change the surface charge characteristics of these soil phases. The effect of pH on M^{2+}cations fixation and release can therefore be thought of as simple competition between protons and M^{2+}cations for the same surface fixation sites in the soil (CWG 2008). The base cations, especially Ca^{2+} and Mg^{2+} and the other M^{2+} cations, exhibit competition effects in the same manner.

However, most metals are sorbed much more strongly to soil than the alkali earth cations (e.g. Ca, Mg, Molloy et al. 2005).

Release of M^{2+} cations to pore-water (and uptake by plants or leaching) can be inhibited by the metal sorption (fixation) to the soil. Metal sorption is influenced by the presence of highly adsorptive solid phases present in the soil, particularly SOM, clay minerals, and Fe and Mn oxides (Alloway 1990), e.g. Cd is most strongly associated with SOM, but other sorptive phases are important. Examples of common processes that may result in fixation or release of Cd are provided in Table 4.2. In general, the strength of Cd fixation increases with each entry down the table.

Table 4.2. Examples of fixation and release for applied soil Cd, a M^{2+} cation (Chaney 2010, Stacey et al. 2010, Kim 2005, Kim & Fergusson 1992).

Immobilisation process	Remobilisation processes	Example of remobilisation
Adsorption to soil exchange sites	Decrease in soil pH; increase in competitive cations; increase complexation agents in soil solution.	Use of Zn-based dithiocarbamate fungicide on crops that supply Zn, which competes with Cd for absorption sites, and a strong Cd complexing agent (dithiocarbamate).
Adsorption to clay minerals.	As above.	Soil acidification through nitrification.
Adsorption to carbonate minerals	As above. Carbonates dissolve more readily below pH 5.	Soil acidification through nitrification.
Adsorption to, and encapsulation within, hydrated soil Fe and Mn oxides.	Fe and Mn oxides dissolve under reducing conditions, releasing their retained metal. Decrease in soil pH.	Seasonal shift to reducing conditions in the subsoil; reducing conditions in the rhizosphere.
Adsorption and chelation by SOM.	Decrease in soil pH. Decomposition of SOM.	Loss of SOM through cropping;
Fixation as a sulphide.	Shift to oxidising conditions.	Ploughing.

So, the main factors which increase the uptake of M^{2+} cations by plants are the amount of M^{2+} cation present, increased acidity (a lower soil pH), a low SOM content, competition with other M^{2+} cations and other cations in general, and increased salinity (CWG 2008), e.g. SOM fixes Cd in the soil, making it less mobile and less phytoavailable with a maximum sorption at about pH 7 (Taylor and Theng 1995, Parfit et al. 1995). However, dissolved organic matter (DOC) could similarly form complexes with M^{2+} cations. Also, M^{2+} cations become more soluble at low and high pH (Strobel et al. 2001). The dominance of pH as a controlling

variable should not be seen as separate from the adsorptive phases, but a master variable that works by influencing the same equilibrium processes.

Nevertheless, increasing the levels of organic matter or other adsorptive phases (particularly Fe and Mn oxides and Al oxides to a lesser extent) tends to lower the release of M^{2+} cations to the soil solution, regardless of pH, and thereby impede uptake to plants (Kabata-Pendias and Pendias 2001). Conversely, when organic matter is lost from soil, M^{2+} cations can become more available for plant uptake (Kim & Fergusson 1992, Figure 4.3). This has implications for horticultural systems and the intensive arable sector, which typically experience declining levels of SOM. In comparison, saline soils can promote greater uptake of M^{2+} cations by plants through formation of soluble M^{2+} chloride complexes (CWG 2008).

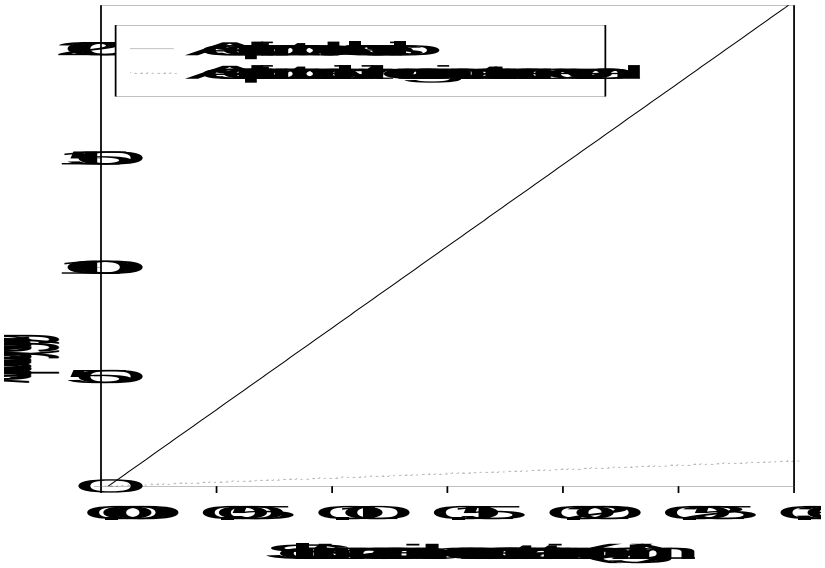

Figure 4.3: Reduction in adsorption of Cd, a M^{2+} cation, to a NZ soil (Tai Tapu Silt Loam) when the SOM is removed (Kim & Fergusson 1992).

4.1.4.2 Cadmium

The priority ranking model ranked Cd from the mineral fertilisers RRP, AP, TSP, SP and blended 6th, 8th, 13th, 23rd and 30th, respectively (Table 3.5). Organic fertilisers derived from plant, cattle, piggery and fish were ranked much lower at 88th, 105th, 106th and 171st, respectively. Cd levels in the organic fertilisers are below background soil values (Table 2.2, Taylor et al. 2014c). As for U, and in the absence of obvious harm to plants and animals, and

their safe use as food, fertiliser made from these materials will likely have minor environmental impacts due to Cd.

Cd is well known as a M^{2+} cation associated with mineral P fertilisers. It is moderately-strongly accumulative in soils from mineral P fertiliser additions (CWG 2008), yet mobile enough for a considerable proportion of added Cd to transfer to water or be taken up by plants. Cd has no known vital biological functions, although a protein that is a Cd-containing carbonic anhydrase from the marine diatom *Thalassiosira weissflogii* has been reported by Lane et al. (2005). Apart from this diatom, high concentrations of available Cd, above critical levels, can be toxic to virtually all forms of animal life, e.g. the provisional tolerable weekly intake for Cd is 7 µg/kg body weight/week for adults (WHO 1992), while the 1:10000 symptom incidence total acceptable daily intake is 9 µg d^{-1} (de Vries et al. 2007a). Cd is considered strongly bioaccumulated by earthworms (Richardson et al. 2015a). Cd is a human and ecological health issue that may suppress soil life (CWG 2008) and is considered a priority contaminant by NZ resource managers.

As expected, elevated median Cd concentration were found in all mineral fertilisers derived from P rock (Table 2.2), up to 12 times soil guideline values for human and environmental health (Appendix 2.11). There was significant accumulation of Cd in NZ soils under all the fertilised land uses assessed in this study (Table 3.7) consistent with studies in many countries including NZ (Schipper et al. 2011, Taylor 1997a, Roberts et al. 1994), Australia (Lottermoser 2009), England (Rothbaum et al. 1986) Ireland (McGrath & Tunney 2010), Spain (Micó et al. 2006), Japan (Yamaguchi et al. 2009, Takeda et al. 2004), Canada (Sheppard et al. 2009b), Argentina (López Carnelo et al. 1997) and the Czech Republic (Uprety et al. 2009). Levels of Cd were such that many farms exceed the tier 1 values (1 mg kg^{-1}) of the NZ Cadmium Strategy (CWG 2008) and required increased soil testing as well as use of low-Cd fertilisers.

The highest soil sample, of 2.14 mg kg^{-1}, was due to Cd derived from a power pylon and was an outlier. It does highlight another source of Cd, Cd impurities in Zn coatings used on metal structures. While this is an important contribution of localised contamination within 2 m of

the structure, it is of limited importance at larger scales and unlikely to impact on the results of this study. Most of NZ does not have metal structures on the land, so Cd from Zn coatings is likely a minor source compared to Cd from mineral P fertilisers.

The highest median Cd concentration in soil was in kiwifruit orchards, which are a high intensity crop so receive high P fertiliser inputs, e.g. applications of 1 t ha^{-1} superphosphate or RRP + mixtures of "organic inputs" were recorded at some of these sites. The large applications of RRP to organically farmed kiwifruit and corresponding elevation in soil Cd concentrations may be of particular concern to organic kiwifruit growers.

The overall estimated application of Cd as SP was 0.98 mg kg^{-1}, considerably more than the 0.30 mg kg^{-1} measured accumulation in the top 10 cm of soil. However, mixing by ploughing and soil organisms will increase the depth of soil impacted by Cd. Even allowing for this deeper mixing, it appears a considerable proportion of Cd has been lost.

Once it is accumulated in soil, depletion of Cd occurs slowly by plant uptake, removal in livestock, leaching and erosion (Schipper et al. 2011, McDowell 2010, Gray et al. 2003, Loganathan & Hedley 1997). High levels in soils increase the risk that Cd will enter the human food chain. Some plants, such as potatoes, wheat and green leafy vegetable, can take up Cd in excess of food standards (CWG 2008). Excessive levels of Cd in food can have implications for human health and excessive levels of Cd in soils can restrict land use flexibility (CWG 2008).

Other factors that increase uptake of Cd by plants are Zn deficiency in soils and greater aeration, e.g. anaerobic conditions reduce the uptake of Cd by plants (Chaney and Hornick 1978). However, where Zn is adequate or above adequate requirements, completion with Cd influences the equilibrium processes, and may reduce plant uptake, e.g. a large amount of Zn is added to soil via animal excretion during preventative treatments for fungal diseases and it is also present in a wide range of other agricultural chemicals. Zn competes with Cd for both adsorption sites in the soil and uptake through plant root cell membranes. The impact of Zn may therefore be to increase Cd in porewater, but decrease uptake into plants (Alloway 2008).

Although Zn tends to result in decreased Cd uptake, this type of interaction is complex and such an effect is not always evident under actual field conditions (Nan et al. 2002).

Plant-related factors that influence the uptake of Cd include: the crop species and cultivar; the types of plant tissue; leaf age and metal interactions. The older the age of the plant, the more Cd it will contain. Alternatively, soil ingestion may also be a significant source of animal uptake of Cd if there is a lack of grass cover (CWG 2008).

Some of the applied Cd appears to leach, consistent with Tyler (2004c) who showed some Cd had been lost from 4 soil profiles for a podzol soil, along with alkaline-earths, REEs, U, and some other M^{2+} cations. Although concentrations of soluble Cd are influenced by total soil Cd, soil pH and SOM (Gray et al. 1999, Gray & McLaren 2006), modelling Cd leaching in NZ appears largely unsuccessful due to the influence of other factors. Instead, leaching of Cd appears to be soil specific as there seems to be a higher risk of leaching in certain soils, e.g. high mobility of Cd has been observed in sandy soils (McLaughlin et al. 1996). A comprehensive attempt to understand Cd leaching was presented in Gray et al. (2003). They found a wide range of Cd leached, spanning 0.27 to 0.86 g ha^{-1} y^{-1} but no statistical relationships between the amounts of Cd leached and major soil characteristics were established.

Aeration results in the faster oxidation (breakdown) of SOM, potentially causing its adsorbed Cd to be released. This is partly through increased microbial activity stimulated by fertiliser addition. As a secondary effect, increased microbial respiration associated with aeration may result in higher partial-pressures of carbon dioxide in porewater, which would reduce the pH (Weihermüller et al. 2007). Aeration may therefore act via SOM and pH. Conversely, anaerobic conditions inhibit the oxidation of SOM. However, in cases where Cd is mainly bound to soil Fe and Mn oxides (e.g. when organic matter content is low), anaerobic conditions may work to cause its release, by causing the metal oxides to be chemically reduced, i.e. Fe^{3+} becomes dissolved Fe^{2+} (CWG 2008).

Soil properties that affect Cd availability in soil are important because of significant and complex soil-plant, soil-water and soil-organism relationships (de Vries et al. 2007b). Critical concentrations of Cd in the soil are driven by food quality, drinking water quality and acceptable intake by soil organisms and bioaccumulation, e.g. intake of worms by worm-eating birds and mammals. If enrichment of Cd continues, food standards for some crops and animal products are likely to be exceeded, restricting land use and farm production, and resulting in contamination of the wider environment; soil, surface and ground waters, and restricted aquatic environments, e.g. estuaries and lakes.

Some microorganisms, fungi and worm-eating animals are very sensitive to metal inputs including Cd (Alloway 2008, de Vries et al. 2007b, Chaudri et al. 1993). Agriculture production systems that rely more heavily on plant–microbe symbioses (e.g. *Rhizobium*, mycorrhizae), such as NZ's clover-ryegrass system, may be at risk of adverse impacts.

Consistent with the leaching of Cd, elevated Cd levels were identified in some groundwater bores in areas of intense farming (Hadfield 2011, Figure 3.6). However, the maximum level was still only ½ the drinking water standard for NZ of 0.00005 mg L^{-1} (USEPA 2004) and well below the trigger value for freshwater protection for 95% of species is 0.0002 gm^{-3}, (ANZECC 2000). In comparison, Tables 3.10 and 3.12 showed Cd in surface water was below detection. There is currently minimum risk to human and animal health from Cd in drinking water but this assessment will need revision if levels in groundwater increase.

Dune lake sediments and estuarine sediment from sites on the west coast of the Waikato region and sites from the Wellington, Tasman and Southland regions were similar and had very low Cd concentrations, less than concentrations found in background soil (Table 3.15). However, sediments in peat and riverine lakes and from the Firth of Thames, particularly at the mouth of the Piako River, showed considerable elevation, suggesting appreciable transfer of Cd from land to sediments. The Piako River catchment includes a large area of peatland and peat lakes had the highest Cd concentrations, suggesting peat and organic soils may have limited capacity to hold Cd. One mechanism of transfer may be as complexes with DOC as organic carbon and Cd were highly correlated (Spearman Rank Correlation r = 0.56, Table

3.16). However, Cd had a higher association with Al (Spearman Rank Correlation r = 0.72), so most Cd in lake sediments in likely in an inorganic form, presumably adsorbed on to the surfaces of Al minerals. PCA also showed Cd to be in the component associated with Al (Table 3.16). Conversely, PCA of estuaine sediments showed Cd to be in the component associated with organic carbon (Table 3.18) with a Spearman Rank Correlation of r = 0.66.

Adsorbed cations can be released back into solution, e.g. by physical disturbance or increase in alternative exchangeable cations, while organic matter can be oxidised to CO_2. The accumulation of Cd in sediment may be considered a potential source of Cd. Some management activities, in particular dredging, may release Cd (and other metals) back into the water column. Impacts on the marine environment, such as high uptake of anthropogenic Cd by plankton communities have been reported (Augar et al. 2015). Thus, consideration of environmental effects is needed by water managers before carrying out activities that may significantly increase the release contaminants from sediments back into water.

In response to concerns about the likely continued accumulation of Cd in NZ soils, the Cadmium Working Group (CWG), consisting of representatives from NZ industry, food safety, environment, regional councils and local communities, assessed the current status of Cd in agricultural soils, and identified potential risks to human health, trade and the economy, and flexibility of land use (CWG 2008). Tasked with developing responses to potential risks, the working group developed a strategy for managing Cd over the long term. This management strategy outlines a combination of governance, research, monitoring and management for food, soils and fertiliser (CWG 2011). It is intended to stand until 2018 whilst information is collected and research undertaken to fill key knowledge gaps, with the aim of a review at the end of this period to determine progress and future directions. A governance group, the Cadmium Management Group, is charged with implementing this strategy.

The Cadmium Management Group recommends that to reduce cadmium uptake into food crops phosphate fertilisers with low levels of Cd should be used, along with maintaining soil pH at the upper recommended limits for crop type and maintaining high SOM. It also

recommends alleviating any Zn deficiency in the soil, minimising, and avoiding if possible, the use of acidifying fertilisers, and to avoid fertilisers and irrigation water containing high levels of Cl (CWG 2008, McLaughlin et al. 1996, Chaney and Hornick 1978).

The accumulation rate for Cd was estimated by dividing the difference between BG soil in NZ and the median concentration of all fertilised sites (0.30 mg kg^{-1}) by the estimated time fertiliser had been applied (65 y). This gave an accumulation rate of 0.0046 mg kg^{-1} y^{-1}, compared with the rate of 0.0065 mg kg^{-1} y^{-1} for a NZ soil reported by Rothbaum et al. (1986). On the other hand, Taylor (1997a, 1994) reported higher accumulation rates of 0.010 mg kg^{-1} y^{-1}. The lower accumulation rate reflects the reduction in Cd concentrations found in modern mineral P fertilisers used in NZ.

In NZ, Cd accumulation in soil has been reported to be minimised if the concentration of Cd in the applied phosphate product is low, e.g. less than 5 mg kg^{-1} (CMG 2011). This is the level at which inputs of fertiliser associated Cd should balance outputs in production and to water. The Minimal Risk Guideline Value, below which ecological risks may be coinsidered tolerably low, should be met (CMG 2011, Cavanagh and O'Halloran 2006) if soil concentrations are kept below 1.0 mg kg^{-1}.

4.1.4.3 Zinc

The priority ranking model ranked Zn in fertilisers made from piggery, poultry, TSP, RRP, fish, plants, AP, SP, blended and cattle 19^{th}, 24^{th}, 29^{th}, 41^{st}, 44^{th}, 45^{th}, 53^{rd}, 56^{th}, 63^{rd}, 66^{th}, respectively (Table 3.5). Median Zn concentration in all fertiliser types tested exceeded background soil values by about 2.5 or more (Table 2.2, Taylor et al. 2014c). This observation suggests fertiliser impurities ranked $<67^{th}$ in Table 3.5 may have some impact on environment.

Median Zn concentration in all fertilisers types tested (110-790 mg kg^{-1}, Table 2.2) exceeded environmental guidelines by 2-12 times (plants 64 mg kg^{-1}, microorganisms 100 mg kg^{-1}, Appendix 2.11). As expected, the fertilisers with the highest Zn concentrations were those

derived from organic materials, especially those from piggery (790 mg kg^{-1}) and poultry (360 mg kg^{-1}) products. Thus, fertilisers appear to be a substantial source of Zn to fertilised soil.

Zn is essential to plants and animals, and it ranks as the third most important limiting nutrient element, next to N and P, in crop production (Gowariker et al. 2009). However, excessive Zn concentrations have high toxicity to microorganisms and some plants, and are considered a priority contaminant by NZ resource managers (Kim & Taylor 2013, Kim 2005). Zn is also considered strongly bioaccumulative by earthworms (Richardson et al. 2015a).

Unlike Cd, F and U, there are multiple major sources of Zn contamination to the environment. Sources in NZ include mineral and organic fertilisers, 369 veterinary medicines, 35 registered pesticides, galvanised (Zn coated) iron, Zn paint, tyre rubber and human sewage discharges. Manures and poultry litter has been reported to contribute significant amounts of Zn (Bolan et al. 2010, 2004, Luo et al. 2009, Uprety et al. 2009, McBride & Spiers 2001, Mortvedt 1995). The veterinary medicines are recorded in a register of veterinary medicines, animal remedies and plant compounds maintained by the New Zealand Food Safety Authority, while a register of licensed pesticides is maintained by the Environmental Risk Management Authority New Zealand.

One other major source in NZ is likely to be the treatments and preventatives of the fungal disease facial eczema (Figure 4.4). This one source is estimated to contribute about 8500 t of Zn per year to the environment in the Waikato region (Kim 2005). Preventive treatment includes dosing animals to subtoxic levels with Zn, either in drinking water, as boluses or directly injected.

Figure 4.4: Examples of the fungal disease facial eczema. Dosing animals with Zn prevents this decease (Waikato Regional Council).

While Zn in waters is generally considered not very toxic to macro-biota (Kabata-Pendias & Murkherjee 2007), soil organisms appear more vulnerable to Zn toxicity than aquatic organisms. Also, soil microorganisms and invertebrates tend to be more susceptible to Zn toxicity than higher plants because they have less well developed homeostatic mechanisms. Results of inhibition of microorganisms and invertebrates include accumulation of litter due to reduced decomposition and the failure of Rhizobium species in nodules on the roots of

legumes to fix atmospheric nitrogen so legume plants and adjacent species show signs of nitrogen deficiency (Alloway 2008). Nitrogen fixing Rhizobia bacteria are relatively susceptible to Zn toxicity and so this economically important group is vulnerable to excessive accumulation of Zn in soil. Reduction in these species would necessitate the increased use of N fertilisers to compensate for the lack of fixed nitrogen with ongoing economic and environmental consequences. Nematodes and enchytraeids are also sensitive to Zn concentrations (Creamer et al. 2008).

Plant species and varieties differ in their susceptibility to Zn deficiency and toxicity, while soil factors and interelement effects are also important. Plants that are susceptible to zinc deficiency are corn, onions, pecans, sorghum, rice, beans, cotton, flax, coffee, citrus and deciduous fruits (Gowariker et al. 2009, Alloway 2008). Conversely, high concentrations of Zn can inhibit many plant metabolic functions, resulting in retarded growth and early senescence. Sensitive terrestrial plants are reported to die when soil Zn concentration exceeds 100 mg kg^{-1} (Kabata-Pendias & Murkherjee 2007), especially in acid soils (Alloway 2008). Excess Zn can also give rise to Mn and Cu deficiencies due to hindered transfer of these micronutrients from root to shoot (Nagajyoti et al. 2010).

Zn was expected to be moderately mobile (K_d typically 450-650, Appendix 2.8) with a proportion of that added accumulating and the rest transferring to water. This was confirmed as results showed Zn to significantly accumulate in NZ soils under fertilised land uses assessed in this study (Tables 3.7-8). This accumulation reflects the Zn applied in fertilisers, veterinary medicines and pesticides. The overall estimated application of Zn as SP was 4.1 mg kg^{-1}, considerably less than the measured accumulation of 39.2 mg $kg^{-}1$ in the top 10 cm of soil. Also, mixing by ploughing and soil organisms will increase the depth of soil impacted by Zn. It is apparent that fertiliser-Zn is a small proportion of the amount applied to soil in NZ.

The accumulation rate for Zn was estimated from the data in this thesis by dividing the difference between BG soil and the median concentration of all fertilised sites (39.2 mg kg^{-1})

by the estimated time fertiliser had been applied (65 y). This gave an accumulation rate of 0.60 mg kg^{-1} y^{-1} from all sources.

Although Zn is quite mobile compared to most other M^{2+}cations in most soils, clay minerals and SOM can bind it strongly, especially at neutral and alkaline pH, and control solubility and bioavailability. While Zn is usually moved down a soil profile due to leaching, plant uptake and subsequent decay readily transports Zn from sub-surface minerals soil to the soil surface (Steinnes & Friedland 2006). SOM can also bind Zn but organo-Zn complexes may still be relatively mobile (Kabata-Pendias & Murkherjee 2007), e.g. Zn in soil solution in a slightly acid loamy fine-sand was attributed to manure from grazed cattle (Anguelov & Anguelova 2009) probably as organo-Zn complexes of Dissolved Organic Matter (DOM).

The result of these complex interactions is an uneven distribution of Zn accumulation in soils, with the highest background contents expected to be in the more alkaline soils and soils with high SOM. So, soil is acting as a sink and a source for Zn. Both the accumulation of Zn in soil and the increase in surface water Zn concentrations can be explained by the characteristics of Zn in soils. However, soils are dynamic and changes in land use that result in change to soil properties can impact strongly on Zn toxicity or deficiency, e.g. allowing a neutral/alkaline soil to become acid may induce Zn toxicity as maximum Zn uptake by plants occurs at low soil pH. Conversely, Zn deficiency in plants can result from overliming (Gowariker et al. 2009, Alloway 2008).

Consistent with the prediction and literature (Richardson et al. 2015b, Tyler 2004), some of the applied Zn appears to leach from soil to groundwater and surface water, and this transfer of Zn to water appears associated with farming intensity. Zn in surface waters appeared higher in the high intensity dairy farming areas of the Waikato Region than in the traditional sheep farming regions of Marlborough and Wellington. Concentrations were highest in Lake Ngaroto, a peat lake, suggesting peat had poor sorbtion of Zn or the movement of Zn in DOC to the lake (Tables 3.10). Zn levels in groundwater were higher in regions with higher P fertiliser and Zn-animal remedy use. Levels in groundwater bores were higher in the Auckland Region (median 0.021 g m^{-3}), than the Waikato and Wellington regions (0.010 and

0.007 respectively, Table 3.21). Auckland Region is urban dominated by Auckland city, which contains $^1/_3$ the population of NZ. In comparison, bores in land under agricultural land in Taranaki, with similar farming intensity and soils to the Waikato, were reported to range from 0.001 to 0.33 g m^{-3} (TRC 2013a, b, c, d, 2012, 2008).

Zn concentrations were lower in lake waters than in rivers and streams (Table 3.10). Individual measurements for streams and rivers were also much more variable with values over 3 orders of magnitude although the vast majority of measurements were low (Appendix 3.1). High values were attributed to flood conditions with high sediment loads.

Median Zn concentrations were elevated in nearly all sediments. Higher concentrations were in Waikato Region lake sediments and estuarine sediments from the Firth of Thames than in estuarine sediments from the west coast of the Waikato region and estuarine sediments from the Wellington, Tasman and Southland regions (Tables 3.15). The highest median concentration was for peat lakes (146 mg kg^{-1}) and for estuarine sediments from Appletree (124 mg kg^{-1}) and the Piako River mouth (104 mg kg^{-1}), which receive inputs from peat land. Thus, it is likely that peat had poor sorbtion of Zn and Zn was transported attached to DOC to the lake, where the high levels of Fe and Al minerals in the bottom sediment, as evident from concentrations in Table 3.15, provide abundant sorption sites.

PCA of lake sediments showed Zn to be associated with Al on component 1, with a Spearman's rank correlation of r =0.62 (Table 3.16-17). Zn is easily accumulated in bottom sediments of lakes, rivers and estuaries from the erosion of soil particles containing Zn and adsorption of dissolved Zn (Kabata-Pendias & Murkherjee 2007). PCA of estuarine sediments showed a more complex picture for Zn with components 1, associated with Al, 2, associated with OC and Mn and 3, associated with Mo, Hg, Pb, Cu, Co, As and Sb, having moderate loadings. Spearman's rank correlation showed Zn to be correlated with OC (r = 0.66), Al (r = 0.68), Fe (r = 0.75) and Mn (r = 0.90).

Zn is essential for animals and it must be supplied continuously in the diet because it is not stored in the body. However, the amount needed varies depending on species, age, and health

condition of the animal. While most animals can tolerate high Zn diets, horses are more sensitive to excess Zn (EC 2003). In humans, Zn has low toxicity so deficiency is more common than toxicity. Therefore, the relatively low concentrations of Zn in mineral P fertilisers are likely beneficial to farmed animals in the NZ environment. However, care must be exercised where mineral fertilisers are fortified with Zn and with organic fertilisers made from high Zn containing raw materials to not apply these in excessive amounts, especially where other Zn sources are used, e.g. facial eczema treatment.

The magnitude of Zn application is likely to increase if mineral P fertilisers were replaced to any large extent by organic fertilisers derived from piggery and poultry products. However, Zn impacts on nitrogen fixing legume/grass pastures should be made clear before changing fertiliser regimes.

4.1.4.4 Copper

The priority ranking model ranked Cu in fertilisers made from piggery and poultry products 35th and 40th. Fertilisers made from SP, plant, AP, TSP, cattle products and blended were <2.5 times background soil Cu concentrations and ranked 73rd, 75th, 79th, 89th, 90th, 108th, consistent with fertilisers generally being a minor source of Cu to soil (Table 2.2, Taylor et al. 2014c). These rankings suggest only fertilisers made from piggery and poultry products have sufficient Cu to have significant environmental or health effects. Although higher concentrations of Cu were found in fertilisers derived from piggery products (200 mg kg^{-1}), up to 3½ times soil guideline values for human health and ecological receptors (63 mg kg^{-1}, Appendix 2.11), these concentrations were considerably lower than the 500-1000 mg kg^{-1} reported by McBride & Speirs (2001). However, concentrations were more than 10 times those found in background soils (Table 2.2). Also, poultry products had Cu concentrations 4-5 times background soil concentrations.

Cu is essential for the growth and development of higher plants, terrestrial mammals, aquatic organisms and some algae, but may become toxic at higher concentrations and is considered a priority contaminant by NZ resource managers.

Like Zn, there are multiple sources of Cu besides fertilisers including a large number of agricultural and horticultural chemicals, timber treatment chemicals, copper piping and guttering, and vehicle brake linings, e.g. Cu was commonly used in NZ and Australia as a ‘‘growth promoter’’ in piggery production and manures may contain from 500–1000 mg kg^{-1} of Cu (McBride & Speirs 2001). A substantial accumulation of Cu from the use of piggery products has been noted by previous studies (Eriksson 2001, Chang & Page 2000).

Accumulation of Cu in soil increases baseline dietary uptake of animals from plants and direct ingestion of soil. While Cu toxicity in animals has been reported if Mo intake is too low (Section 4.1.8), Cu toxicity has also occurred in NZ where dairy cows have been dosed with Cu to avoid deficiency but then fed palm kernel as a supplementary feed product. Palm kernel can have high concentrations of Cu and this, combined with the direct Cu dose, induced copper toxicity (Dias 2010). No corresponding problems in humans have been reported.

Despite Cu tolerance in plants generally, this element is considered to be quite toxic (Kabata-Pendias & Murkerjee 2007). Many complex interactions of Cu with other elements are observed within plant tissues, e.g. accumulation of Cu in *Azolla* was correlated with damage caused by the loss of the essential nutrients K, Cl, and Mg (Sela et al. 1988). Similarly, Cu and Zn apparently are absorbed by the same mechanism and therefore each may competitively inhibit root absorption of the other (Steinnes 2009, Kabata-Pendias and Pendias 2001). In addition, hindered transfer of these micronutrients from root to shoot also occurs (Nagajyoti et al. 2010). Cu also interferes with the role of Mo in the enzymatic reduction of nitrate aggravating Mo deficiency in plants where deficiency already exists (Kabata-Pendias and Pendias 2001).

Conversely, Cu deficiency most commonly occurs in coarse structured soils with high pH, and/or calcareous soils, and/or in soils rich in organic matter. Cu deficiency in crops is widespread and often not recognised. Alloway (2008) stated this undetected form of Cu deficiency in crop plants is the most ubiquitous and economically important, and is a more serious problem in Europe than in many other parts of the world, e.g. 25% in Germany have Cu concentrations that can result in Cu deficiency in sensitive crops such as cereals, spinach

and lucerne (Kabata-Pendias & Pendias 2001). Cu deficiency may be an issue for unfertilised soils in NZ due to their high organic content, but normal farming practices, including additions of fertiliser, make deficiency unlikely.

Cu was predicted to accumulate in soils (K_d typically 800-1000, Appendix 2.8). However, Cu is also moderately mobile in soil and a significant proportion was expected to transfer to water. Tables 3.7-8 showed Cu to significantly accumulate in NZ soils under fertilised land uses, except for pasture used for meat production, which had similar Cu content compared to background soil. The overall estimated application of Cu in SP was 0.88 mg kg^{-1}, considerably less than the measured accumulation of 6.0mg kg^{-1} in the top 10 cm of soil. Also, mixing by ploughing and soil organisms will have increased the depth of soil impacted by Cu and decreased concentrations. It is apparent that fertiliser-Cu is a small proportion of the amount applied to soil in NZ.

The accumulation rate for Cu was estimated from the data in this thesis by dividing the difference between BG soil and the median concentration of all fertilised sites (6.0 mg kg^{-1}) by the estimated time fertiliser had been applied (65 y). This gave an accumulation rate of 0.0.092 mg kg^{-1} y^{-1} from all sources.

NZ soils, generally, have relatively high total C and therefore high SOM contents, and slightly acid to near neutral pH, conducive to Cu retention (Appendix 1.2). The level of accumulation was much greater in soils under horticulture. The main land use contributors to these higher soil concentrations were pipfruit (apple and pear) orchards, which use Cu fungicides to protect fruit from black spot fungus. So Cu from fertilisers appears a minor contributor to the total soil Cu load for this land use.

Consistent with leaching, Cu in the more acid soil under (usually unfertilised) forestry land use was significantly depleted compared to BG soils. The increased soil acidity under pine forestry may also contribute to increased Cu mobility, while the organic matter under pine forest may be a significant source of DOC.

The mobility of Cu is especially tied to that of SOM, which is important for NZ's highly organic soils, e.g. if the SOM is immobile, so is Cu complexed with it. However, the DOM fraction of SOM is mobile and has a great affinity for Cu, thus inhibits its sorption onto the soil matrix. Cu concentrations in soil extractions were inversely related to SOM (McGath et al. 1988), while the most common form of Cu found in soil pore water was complexed and strongly correlated with DOM (Hough 2010, Linde et al. 2007, Berggren 1992). Historical accumulation of Cu in agricultural soils is a source of contamination to shallow groundwater and surface water in the Netherlands (Schipper et al. 2008) and the highest leaching rates could be expected from the wet peat areas and in agricultural regions with intensive horizontal drainage systems. Thus, leaching of Cu from agricultural land can be an important source of surface and ground water contamination in many countries (Richardson et al. 2015).

Median Cu concentrations in surface waters were lower in the Waikato region than those in the Marlborough region (Table 3.10). In the Waikato region, highest concentrations were in Lake Ngaroto, a peat lake, consistent with movement of Cu in DOC from peat land to the lake. The Cu trigger value for freshwater protection for 95% of species is 0.0014 g m^{-3} (ANZECC 2000) and this was exceeded in half the samples taken from this lake. However, this is the value for slightly impacted waters and only one samples exceeded the trigger value for 90% protection (0.0018 g m^{-3}).

On three occasions, Cu concentrations in two riverine lakes were also above the Cu trigger value for protection of 95% of species. However, measurements were highly variable and the majority of riverine lakes had Cu concentrations below guidelines.

In comparison, Cu in Waikato River samples were below detection until the river received urban inputs from Hamilton City, which was attributed to this city's discharge of stormwater (Table 3.12). Also, a large contribution of Cu came from the Waipa River, which flowed through moderately intensive meat production farm land before joining the Waikato River. A large proportion of the soils in the Waipa River catchment are derived from sedimentary material and the sediment load of this river is much higher than that in the Waikato River

(Figure 4.5), suggesting particle transfer from erosion as a transport mechanism as well as Cu transport in DOC.

Figure 4.5: Confluence of the Waikato and Waipa rivers. The Waipa River has a naturally higher sediment load due to the presence of higher clay content, sedimentary derived soils in its catchment (Waikato Regional Council).

PCA of Waikato lake water data showed Cu to be highly loaded on component 3 along with Mn, Co and Zn. In comparison, PCA of Waikato River water data showed Cu to be moderately loaded on component 3 along with Ca and Sr. As organic matter data was not available for these waters it is not possible to say if Cu was associated with DOC or not.

However, lakes sediments showed only a slight enhancement of Cu, up to two times background soil concentrations, while estuarine sediments from the Waikato, Wellington, Tasman and Southland regions all had similar or lower concentrations to background soils (Table 3.15), so these are not acting as a sink for Cu.

PCA of Waikato lake sediments showed Cu to be moderately loaded on components 1 (0.399) along with Al, component 2 (0.425), component 5 (0.497) along with Zn, and component 6 (0.450, Table 3.16). However, Spearman's rank correlation did not show high correlation between Cu and any of these elements (Table 3.17). In comparison, PCA of Waikato estuarine sediments showed Cu to be highly loaded on component 3 along with Sb, As, Co, Hg, Mo, Pb and Zn. Spearman's rank correlation showed Cu correlated with Al (r= 0.66), Fe (r=0.71) and Mn (r=0.76), but not with OC. These results show Cu has become decoupled from OC and adsorbed onto inorganic components.

The lack of enhancement in the NZ estuarine sediments is surprising as Cu is known to transfer from soil to estuarine sediments, either attached to aluminosilicates (Windom et al. 1989) or attached to organic matter (Calmano et al. 1988). Dissolved Cu is also known to be scavenged by Fe-oxyhydroxides in coastal sediments and released when the Fe-oxyhydroxides are reduced (Kalnejais et al. 2015). However, it appears Cu in the water column is remaining suspended and not adsorbing onto sediments for these NZ estuarine sediments. Another factor may be that the mangroves growing in some estuaries are taking up Cu. Preda & Cox (2002) reported Cu does not occur in significant concentrations in sediments under mangroves, but it was always present in mangrove tissue. Trace element contents in mangrove follow the order: Cu > Pb > Cd > Zn with Cu and Pb accumulating in root tissue to levels higher than surrounding sediment concentrations, while Zn was accumulated to levels reflecting sediment concentrations (Jia-En et al. 2010, McFarlane et al. 2003).

Enrichment of Cu in river and lake water may be of interest to the trout fishery in NZ as rainbow trout, *Oncorhynchus mykiss*, showed severe impairment of branchial ionoregulatory capacity caused by Cu. Specifically, some aspects of gill ion transport (specifically the apical Na^+/NH_4^+ and Cl^-/HCO_3^- exchanges involved in acid/base regulation and nitrogenous waste excretion) were vulnerable to inhibition in the presence of waterborne Cu (Wilson & Taylor 1993).

Median Cu concentrations were similarly low in ground waters from the Waikato, Auckland, Taranaki and Wellington regions (Table 3.21). Cu levels in private groundwater bores in the

Waikato region ranged from <0.005 to 0.022 g m^{-3} (Hadfield 2013, 2011), while under agricultural land in the Taranaki region Cu values up to 0.02 g m^{-3} were detailed in consent monitoring reports (TRC 2013a, b, c, d, 2012, 2008), but these levels could also be attributed to geological or anthropogenic sources.

Like Zn, the low concentrations of Cu in mineral P fertilisers on their own are likely beneficial in the NZ environment. However, they do add to the Cu burden in the agricultural environment and care must be exercised to not apply high Cu containing organic fertilisers or Cu fortified mineral fertiliser in conjunction with other Cu sources, e.g. Cu-fungicides. Consideration of the source of Cu and a mass balance should be carried out before application of high Cu products to land.

4.1.4.5 Mercury

The priority ranking model ranked Hg derived from products of fish 80th, poultry 166th, piggery 177th, cattle 178th and plants 185th, while Hg derived from mineral P fertilisers ranked SP 175th, RRP 176th, AP 162nd, TSP 165th and blended 184th (Table 3.5). Median concentrations of Hg in fertilisers are relatively low (0.01 – 0.66 mg kg^{-1}, Table 2.2, Taylor et al. 2014c) compared to many other trace contaminants found in fertilisers. Higher concentrations were found in fertilisers derived from fish products (median 0.66 mg Hg kg^{-1}) than in other fertilisers examined (median 0.01-0.06 mg Hg kg^{-1}, Table 2.2). These median concentrations were within the range reported by Clifford et al (2010); P fertilisers and manures from 0.01-2 mg kg^{-1} and 0.01-0.36 mg kg^{-1}, respectively. In comparison, the BG soils value for Hg was 0.10 mg kg^{-1}, while the guideline value for plants was 0.3 mg kg^{-1} (Appendix 2.11). So, only Hg in fertilisers derived from fish products had median concentrations >2.5 times the BG soil value and contribute significant amounts of Hg to the soil environment. However, relatively small amounts of fertiliser from fish products is applied in NZ compared to mineral P fertilisers, especially superphosphate (Headly 2011, Table 3.9, Section 3.3.4) and the contribution of Hg from fertilisers to the soil environment can be expected to be similarly small.

Despite the small contribution from fertilisers, Hg is considered nonessential, toxic and bioaccumulative. It has no known vital biological functions and can be toxic to virtually all forms of life and is a priority contaminant for resource managers (Kim & Taylor 2013). All three forms of Hg, elemental, inorganic and organic, can have acute or chronic effects on humans and other higher animals including irreversibly damage to the central nervous system, cancer, intestinal disturbances and death (Clifford et al. 2010). Hg differs from the other M^{2+} metals in that it is a liquid at standard pressure and temperature, so has a comparatively low vapour pressure. The global dispersion of gaseous Hg derived from natural and anthropogenic results in the ubiquitous deposition of Hg to land with volcanic emissions contributing about 20-40 % of this flux (Pyle & Mather 2002). Thus, even Southern Hemisphere soils may be impacted by Northern Hemisphere natural and industrial emissions of Hg.

Estimates of Hg deposition in NZ peat bogs were attempted by Lamborg et al. (2002) but they were unable to accurately date the peat so to give deposition rates. As an aside, tephrachronology of volcanic ash layers common in NZ peat bogs could be utilised to provide dates in such studies (Lowe et al. 2008). Nevertheless, Hg accumulation rates uncorrected for peat accumulation/decomposition ranged from about 1-40 µg m^{-2} y^{-1}. In comparison, the Pb^{210} corrected accumulation rates in NZ lakes varied with each lake and ranged from 2-47 µg m^{-2} y^{-1} (Lamborg et al. 2002). However, there appears to be a wide range of technical difficulties with correcting accumulation rates in lakes and peat bogs including the contributions of location, climate, localised sources such as volcanic eruptions, catchment effects such as erosion and deposition, sediment focusing, preferential mobilisation and transport of Hg, in-lake productivity, peat growth/degradation rates and smearing of Pb^{210} concentrations which are used in dating peat (Hermanns & Biester 2013a, Biester et al. 2007, Biester et al. 2003), suggesting accumulation rates so estimated may be prone to considerable uncertainty.

Accumulation rates for Hg in countries of similar latitude could be expected to be similar, so Chile and Canada should be suitable proxies for NZ. Accumulation rates of about 1-7.9 µg Hg m^{-2} y^{-1} were measured in Chilean peat bogs (Hermanns & Biester 2013, Biester et al. 2002a, 2003). The lower rates are the historic background, while the higher rates reflect modern global Hg deposition. In addition, the likelihood of errors decreases if estimates can be made

comparing several different methods. Rates in rain collections and accumulation rates in bogs and lakes of 8, 8 and 11 µg Hg m^{-2} y^{-1}, respectively, were measured in Nova Scotia, Canada (Lamborg et al. 2002).

Accumulation from the global flux of Hg will occur in background soils as well as the various land uses of Table 3.7. However, forest canopies can also intercept Hg gas and transfer it to the forest floor in litterfall (Filippelli et al. 2015). The addition of Hg from fertilisers and from other sources is thus able to be differentiated from the global component only with some uncertainty. Other sources of Hg in NZ include burning fossil fuels, geothermal power generation, industrial wastes and sewage (Clifford et al. 2010). Past sources of Hg are pesticides, gold and silver mining.

Hg applied to soil, from all sources, was expected to accumulate (K_d measurements typically 4000-6000, Appendix 2.8). However, Hg differs from other M^{2+} cations due to its rapid reaction with soil constituents and its tendency to hydrolyse (McLaughlin et al. 1996, Thanabalasingam & Pickering 1985), e.g. under eutrophic conditions and in the presence of hydrogen sulphide, mercury ions form relatively insoluble mercurous sulphide. On the other hand, if the environment changes to aerobic conditions, mercurous sulphide oxidises to more soluble mercuric sulphate, while bacterial activity can form methyl-mercury (Hg-me, Nagajyoti et al. 2010).

Tables 3.7-8 showed Hg had significantly accumulated in soils under intense vegetable production, consistent with Zheng et al. (2008) who reported fertiliser application influenced soil Hg concentrations at a long-term experimental station with naturally low soil Hg, and Mirlean et al. (2008) who found Hg concentrations in soil close to a fertiliser factory were up to 32 times those for background soils. However, fish fertilisers are not commonly applied to land under intensive vegetable production.

The overall estimated application in SP in the top 10 cm of soil was minimal, while the measured accumulation of Hg as SP was 0.20 mg kg^{-1} (Table 3.8). Also, mixing by ploughing

and soil organisms will increase the depth of soil impacted by Hg but dilute its concentration. It is apparent that fertiliser-Hg is a small proportion of the amount applied to soil in NZ.

The accumulation rate for Hg was estimated from the data in this thesis by dividing the difference between BG soil and the median concentration of all fertilised sites (0.20 mg kg^{-1}) by the estimated time fertiliser had been applied (65 y). This gave an accumulation rate of 0.0030 mg kg^{-1} y^{-1} from all sources.

Hg has been reported to occur in SP due to its addition as a contaminant of sulphuric acid used to acidify the raw phosphate rock during production (McLaughlin et al. 1996). Thus it was somewhat surprising that concentrations in SP measured in this study were below concentrations measured in background soil.

Another possible source is the historic use of Hg-based fungicides and seed coatings, which were banned in the 1970's (Clifford et al. 2010). These soils have been in vegetable production since about the middle of the 19^{th} century. If historic fungicides and seed coatings were the source of the enriched Hg, it would mean Hg is strongly held onto the soil and relatively immobile. This could be a reasonable explanation as many of the soils used for vegetable growing have naturally high Fe and clay contents, which provide sorption sites for Hg and retard leaching (Craw 2005, Franzen et al. 2004, Biester et al. 2002b, Roulet et al. 1998).

Figure 4.6 shows the strong relationship between soil Fe and Hg for nearly all these vegetable production sites. A separate cluster were six vegetable production sites owned by the same family company, which had only moderate soil Hg concentrations (about 0.3 mg kg^{-1}), although they had high to very high Fe concentrations (about 60000-80000 mg kg^{-1}). These were removed as outliers. That these 6 sites had moderate soil Hg despite the high soil Fe concentrations, yet were surrounded by other vegetable producing sites with high Hg concentrations shows the accumulation of Hg in the soil cannot be attributed solely to global Hg deposition.

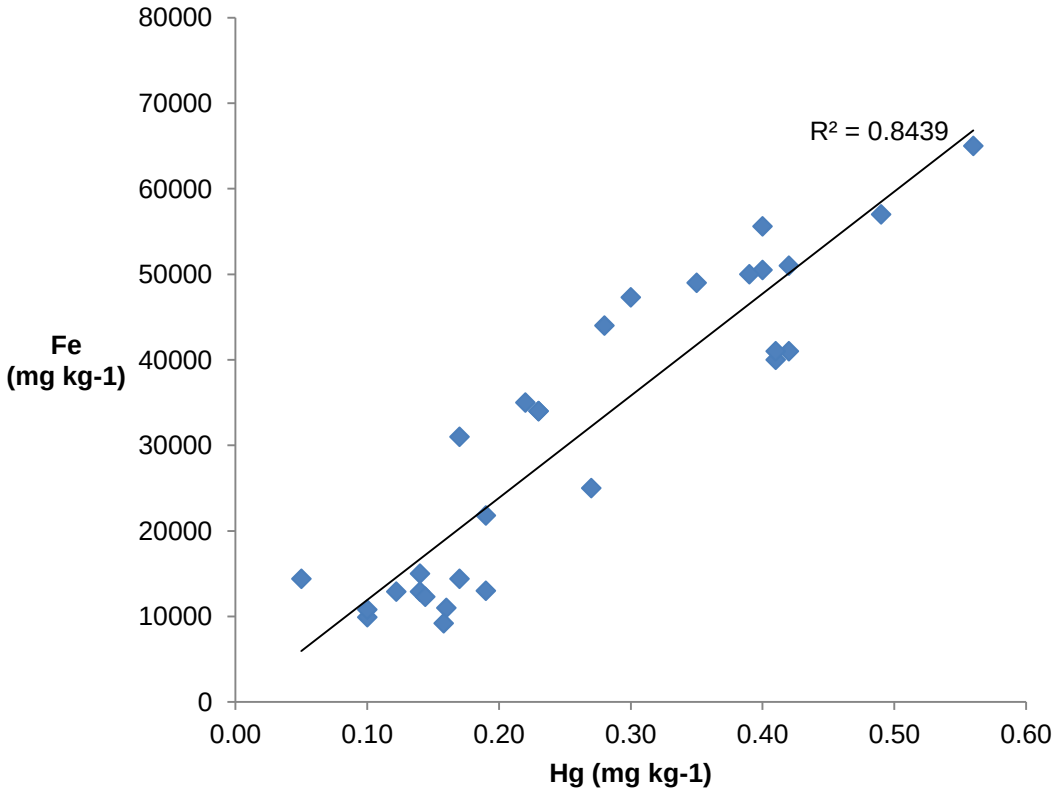

Figure 4.6: The relationship between Hg and Fe in soils used for vegetable production. Six sites with moderate and high concentrations of Hg and Fe, respectively, were removed as outliers.

The effects from Hg concentrations in vegetables grown on these intense vegetable production sites are likely to be minor as the availability of soil-bound Hg to plants is usually low and mostly accumulates in the plant roots (Tyler 2004b, McLaughlin et al. 1996). However, plant capacity to take up Hg varies, e.g. some plant species, such as lichens, carrots and lettuce, are likely to take up more Hg than other plants grown at the same sites (Kabata-Pendias & Mukherjee 2007). Fungi also vary in their ability to take up Hg; Falandysz et al. (2007) found King Bolete mushrooms (*Boletus edulis*) had up to 130 and 72 mg kg^{-1} in caps and stalks, respectively.

Some plants, such as sugar beets, corn, and roses, are more sensitive to Hg toxicity than others (Kabata-Pendias & Mukherjee 2007). Similarly, some microorganisms are more sensitive to Hg toxicity than others, with adverse effects seen when the soil Hg concentration exceeded 10 mg kg^{-1} (Kabata-Pendias & Mukherjee 2007). This concentration is the threshold

value for the most sensitive organisms. However, concentrations of Hg measured in this study were about an order of magnitude or more less than this threshold value, so adverse effects due to Hg within the soil environment are unlikely.

Nevertheless, additions of Hg to agricultural and cropping land may increase the dietary burden of Hg. While high Hg concentration in fish tissues may be the major source of dietary Hg to the average fish eating person, higher consumption of other foods also contribute to Hg intake and should be considered equally in setting dietary guidelines (Kim & Taylor 2013).

Another consideration is changes in soil pH as inorganic Hg has been reported to leach in neutral and slightly alkaline soils (Kabata-Pendias & Pendias 2001). In comparison, the optimum pH for the adsorption of mercury onto humic substances is 4-5 and that for fixation of Hg on Fe oxyhydroxides is pH 3-4 (de Vries et al. 2007b, Tyler 2004b), so, neutralisation of acid soils is likely to decrease adsorption and enhance mobility of Hg, e.g. development of farmland by clearing forest and adding agricultural lime may mobilise Hg (Craw 2005, Semu et al. 1987). Indeed, Hg concentrations were depleted in soils under pasture and other horticultural land uses compared to background (Table 3.8).

In intensive vegetable production, the pH is already 6.5-7.0, so Hg is unlikely to become much more mobile with pH change. As mentioned, the reason Hg remains elevated in these soils may be related to the high clay content and Fe oxides or Fe oxyhydroxides found in these soils, which provide sites for adsorption (Biester et al 2002b, Kabata-Pendias & Pendias 2001). Also, these soils have already lost much SOM due to decades of tillage (Taylor 2015). Hg can be leached from acid soil profiles as DOM complexes (Linde et al. 2007) or bound to organic S, e.g. CH_3HgS^- (Kabata-Pendias & Pendias 2001), but levels of hot water extractable C and total C for these sites are very low for NZ soils indicating low organic matter. Conversely, leaching of Hg from these soils may also be increased by additions of organic soil amendments that increase DOM.

In neutral or alkaline soil, Hg can be leached in inorganic form if not already bound to the soil matrix, e.g. $HgCl_2$, $Hg(OH)_2$ (Kabata-Pendias & Pendias 2001). DOC may also be important

in Hg transfer as Driscoll et al. (1995) reported concentrations of Hg in lakes increased with increasing concentrations of DOC.

There are several other possible mechanisms for Hg depletion in soils, including podzolisation, transport in DOC, soil erosion and volatilisation. The first three mechanisms could result in transfer of Hg to water while volatilisation would clearly result in transfer of Hg to air.

Podzolization may result in acidic complexation of Hg and subsequent migration to ground or surface waters (Peña-Rodríguez et al. 2014, Tyler 2004c). Podzolisation generally occurs in NZ soils with rainfall >1500 mm y^{-1} (Hewitt 2010). Another mechanism of soil depletion may be erosion of soil, where Hg bound to the soil matrix is transported in particulate form into waterways (Roulet et al. 1998). This would be where surface applied Hg is fixed to topsoil Fe or SOM, which can be transported by wind or water surface erosion. Ryeberg et al. (2014) showed accumulation of Hg in lake sediments reduced drastically when vegetation changed to forest.

Elemental Hg and some forms of organic Hg are easily volatilised due to their high vapour pressure and increases in temperature are likely to increase volatilisation (Chang & Page 2000). Schlüter (2000) reviewed the evaporation of Hg from soils and concluded that low concentrations were released to the atmosphere even from background soils. In NZ, this would be the typical ambient air concentration (0.002 to 0.0004 µg m^{-3}) reported by MfE (2008). As background soils were shaded by the trees growing on them, the background soils were likely to be cooler than soils in agriculture or horticulture and likely to have lower Hg volatilisation (Ryeberg et al. 2014). Microbiological activity can accelerate volatilisation of Hg from soils and form methyl-mercury through the process of methylation. The addition of water significantly increased Hg volatilisation, while saturated soil conditions encouraged methylation (Kabata-Pendias & Mukherjee 2007). Hg vapour may be harmful to plants and soils biota if it reaches high enough concentrations (Kabata-Pendias & Mukherjee 2007) and inhibitory effects increased at 0.014 µg m^{-3} (Seigel et al. 1984).

Hg is not generally measured in surface or ground water quality monitoring in NZ but it was measured in the Waikato River samples presented in Table 3.12 and in two groundwater samples in the Wellington region. Results were below the detection limit of 0.00008 g m^3, well below the NZ Hg guideline trigger value for freshwater protection for 95% of species of 0.0006 gm^{-3} (ANZECC 2000).

Hg was elevated in sediments from the Firth of Thames compared to background soil and median concentrations exceeded the low trigger NZ guideline value for sediments (0.15 mg kg^{-1}), but not the high value (1 mg kg^{-1}, ANZECC 2000). However, Hg was not elevated, compared to background soil, in sediments from dune lake sediments or estuaries from the west coast of the Waikato region or the Wellington region (Table 3.15). Peat and riverine lake sediment Hg concentrations were intermediate.

Transfer of Hg into lake sediments has been previously reported in Driscoll et al (1995) and was expected to be bound to reduced S-groups of the organic matter or precipitated as cinnabar (HgS) (Biester et al. 2007). PCA of lake sediments showed Hg was in the same component as organic carbon (Table 3.16) supporting Hg was bound to the organic matter for these lake sediments. However, PCA of estuarine sediments showed Hg was highly loaded on component 3 along with Sb, As, Bi, Co, Cu, Mo and Zn, and there was no controlling element (Al, Fe, Mn or OC) associated component 3 (Table 3.18). A somewhat similar result was presented by Hermans & Biester (2013b) who proposed this was due to short-term fluxes of organically bound trace elements, which were decoupled from the long term OC flux due to vegetation changes. Major changes in vegetation, from forest to grassland, have occurred across NZ with the arrival of Maoris and Europeans could thus explain the decoupling of Hg and other organically bound elements from OC.

The elevated Hg in sediments from the Firth of Thames may originate from historic mining or historic and continuing decomposition of peat land. A cinnabar deposit occurs near Thames and gold mining occurred over the Coromandel Peninsular on the eastern side of the Firth of Thames. From about 1850-1890 the mercury amalgamation process was used for extracting

Au and Ag until it was superseded by the cyanide process (Nolan 1977). However, this mining only occurred in the eastern Firth of Thames.

In addition, a large part of the catchment of the Piako River, on the south west of the Firth of Thames, is peat land including the Whangamarino Swamp (5,130 ha) and the oligotrophic Kopuatai, Pauarua and Torohape Peat Domes (9,238 ha). Oligotrophic peat bogs receive nutrients and other elements only via aerial deposition, there is no groundwater contribution (Pronger et al. 2014,). Driscoll et al. (1995) reported concentrations of Hg increased with increasing concentrations of DOC and percent near-shore wetlands in the catchment, and concluded that DOC is important in the transport of Hg to lake systems.

There appears no reason why DOC could not be similarly important in the transfer of Hg to the estuarine environment. Peat wetlands are reported to be an important source of methylmercury (MeHg) to aquatic systems where mercury methylation occurs due to the anaerobic conditions that favour sulphate reduction (Mitchell et al 2008). However, watertable changes not only control the decomposition of peat, but they can also allow vertical and lateral flow of trace elements (Waddington & Roulet 1997). Branfireun et al. (2005) reported a ^{202}Hg spike applied to the peat surface was converted to MeHg in situ, and redistributed outside the experimental plot to a depth 15 cm below the water table to a local lake margin along the dominant vector of groundwater flow, within 3 months of application. Thus, additions of inorganic Hg in atmospheric deposition can be readily methylated and transported down the soil profile to shallow groundwater.

Once in groundwater Hg can be transported to the Piako River from peatland by groundwater flow or in drainage channels, and then to the Firth of Thames (Kim & Taylor 2013, Linde et al. 2007). Once Hg reaches the estuarine environment, changes in salinity result in its precipitation or sorption by sediment (Kim et al. 2013).

There appears to have been a substantial transfer of Hg from soil under non-forested land uses to air or water. However, accumulation of Hg in sediments only occurred in some of the lakes and estuaries investigated suggesting specific mechanisms are involved, e.g. DOC in peatland.

Although significant discharge of Hg to lakes or the sea may have health and ecological implications, the concentrations measured in freshwater in this study were very low. However, acidification of waters, such as through increased CO_2 levels in the atmosphere resulting in increased carbolic acid content in water, can increase bioavailability of inorganic Hg (Driscoll et al 1995). MeHg is important as it is highly bioavailable in water and readily accumulated in aquatic organisms, e.g. the majority (95%) of total Hg in fish is MeHg (Kabata-Pendias & Mukherjee 2007). There is a significant and growing aquaculture industry in the Firth of Thames that could, potentially be affected. The consumption of fish containing MeHg is the primary pathway of MeHg exposure in humans (Flippelli et al 2015). High Hg concentration in fish and shellfish tissues is a health risk, especially in populations with high seafood intake (Karatela et al. 2011, Clifford et al. 2010).

Due to the sensitivity of the environment, especially in the marine environment, Hg derived from any source, including P fertilisers, remains a concern for resource managers. However, concentrations of Hg are relatively low compared to many other trace contaminants found in fertilisers and Hg from other sources.

4.1.5 Yttrium, Lutetium and Lanthanides Ce, La, Nd, Y, Sm, Eu, Gd, Dy, Pr, Tb, Tm and Yb

Rare earth elements (REEs) is a collective term for the elements from lanthanum to lutetium, atomic numbers 57–71, in the periodic table. Y chemically resembles the REEs and can be treated as a trivalent REE so is included with REEs group (Kabata-Pendias & Mukherjee 2007, Salminen et al. 2005). All REEs are all strongly electropositive and most of their chemistry is characterised by ionic bonding. The REEs are considered to be biologically non-essential and, although toxicological data are relatively scarce, toxicity is generally considered to be moderate to low (Salminen et al. 2005). However, they can impair cell membranes function in vascular plants and the Ca metabolism in microorganisms (Kabata-Pendias & Mukherjee 2007).

Natural sources of REEs are considered to be more important than anthropogenic ones in the environment as they are constituents of several different minerals and are also likely to be

concentrated in phosphorites (Kabata-Pendias & Mukherjee 2007). These highly insoluble REEs phosphorites form during apatite weathering and may be important secondary sources of P in soils (Cervini-Silva et al. 2005). Anthropogenic sources of REEs include glass, ceramics, electrical devices, fossil fuels, contrast agents used in magnetic resonance imaging, and the steel industry, as well as phosphate fertilisers and manures (Tepe et al. 2014, Kabata-Pendias & Mukherjee 2007, Salminen et al. 2005).

Y and REEs are poorly mobile under most environmental conditions, e.g. the solubility of REES-phosphate salts are very low (Salminen et al. 2005), and they are associated with the 'resistate' group of elements, which includes Zr, Hf and Th. There is a large affinity between REEs and DOM but different types of organic matter have different compexing capacity for REEs (Tang & Johnnesson 2010). In the absence of strong REE complexing ligands in solution, REEs in solution are readily absorbed onto Fe oxides controlled by the surface stability constants for REE sorption with Fe(III) (Tang & Johnnesson 2010) although correlation between La and Al in waters and sediments has also been noted (Salminen et al. 2005).

La was the only REE that had a full set of measurements in both the soil and sediment samples but as REEs have similar chemical behaviour to each other (Tyler 2004a, Baes et al. 1984), and strong to very strong correlations with each other (Salminen et al. 2005), La can be considered representative for the series. However, there were relatively few measurements of La and other REEs in fertilisers (Appendix 2.3)

The priority ranking model ranked La from RRP 25th, SP 64th, blended 75th, AP 98th, poultry 103rd, TSP 107th, Cattle 118th and fish 191st (Table 3.5). Other REE were generally ranked similarly to La or had lower scores so using La as a substitute to assess these elements can be considered conservative. La is considered a low health risk to humans but can be toxic to microorganisms and aquatic organisms (Barry & Mehann 2000), and impact plant growth. The relative root elongation of both mungbean and corn decreased with increasing concentrations of La in solution, while La also caused ruptures to the rhizodermis and the outer cortex of roots in cowpea (Blamey et al. 2010, Kopittke et al. 2008, Diatloff et al. 1995).

La, like U and F, was expected to be relatively immobile in NZ soils due to the predominance of well oxidised, mildly acidic, highly organic soils. REEs were predicted to accumulate more strongly in soil than Cd (typical K_d 2000-12000) and there were high median concentrations of in RRP (100-270 mg kg^{-1}) for those REE where measurements were found (Table 2.2, Taylor et al. 2014c), up to 4 times guideline values (soil organisms 50 mg kg^{-1}, Appendix 2.11). The relative contributions of REE from fertilisers compared to other sources in NZ are unknown.

Tables 3.7-8 showed La to significantly accumulate in NZ soils under fertilised land uses, except for vineyards. The estimated application in SP of La in the top 10 cm of soil was 1.93 mg kg^{-1}, while the measured accumulation of La as SP was 8.35 mg kg^{-1} (Table 3.8). Also, mixing by ploughing and soil organisms will increase the depth of soil impacted by La but dilute its concentration. It is apparent that fertiliser-La is a small proportion of the amount applied to soil in NZ.

The overall accumulation rate for La was estimated from the data in this thesis by dividing the difference between BG soil and the median concentration of all fertilised sites (8.35 mg kg^{-1}) by the estimated time fertiliser had been applied (65 y). This gave an accumulation rate of 0.12 mg kg^{-1} y^{-1} from all sources.

Vineyard soils and soils used for production forestry (usually unfertilised) both had significant depletion of La in soil. Soil pH plays an important role in the stability of complexes, while SOM reduces bioavailability by chelation and directly sorbing La. In addition, high surface area clays can sorb considerable amounts of La (Wu et al. 2001a, b). PCA showed La to be highly loaded on component 2, which was associated with Mn (Table 3.6). The depletion of La under vineyard soil may be due to vineyards in NZ tending to be on stony “poor quality” soils. The abundance of stones >7% of the bulk soil has been identified as a risk factor for increased leaching by increasing by-pass flow (Lilburne & Webb 2002). Furthermore, Tyler (2004a) showed high leaching rates for La in humid environments, such as found in NZ.

La concentrations in stream water were very low, typically <0.0001 g m^{-3}. However, La in water in the peat lake, Lake Ngaroto, was elevated (0.0004 g m^3). Similarly, lake and estuarine sediments measured in this study had slightly elevated La concentrations compared to concentrations for natural background soil (Tables 3.15), except for sediments from peat lakes, which were about 3 times background soil. It is suggested that for peat lakes, REEs are transferred from peat to lake as soluble REEs-DOM complexes (Tang & Johannesson 2010). PCA of all lake waters showed La highly loaded on component 2 and associated with Al and Fe, while PCA of all the lake sediment, showed La to be highly loaded on component 1, which was also associated with Al. This was confirmed by Spearman's rank correlation (r = 0.81) and is consistent with (Salminen et al. 2005). Anthropogenic La in water can be considered bioavailable as it can be incorporated into the shells of freshwater mussels (Merschel & Bau 2015).

The elevated concentrations in the peat lake water and in sediment from a range of peat lakes are consistent with the REEs high-DOC stream water model that is chiefly climate-dominated, where organic matter complexes are the dominant forms in stream water (Salminen et al. 2005). This model gives the distribution pattern of REEs and their numerous associates in high-organic-carbon acid low-mineralisation stream water are mainly controlled by climate, especially rainfall, vegetation and topography. Also, REEs are reported about ten times more abundant in peats than in surrounding mineral soils (Kabata-Pendias & Mukherjee 2007).

La is not currently measured in NZ Regional Council groundwater monitoring samples, and no relevant literature was found so no conclusions on the relevance of fertiliser additions to REEs in groundwater in NZ can be drawn.

There is relatively little ecotoxicity data for REE, which makes justifying guidelines problematic. Until further research is completed, it is suggested that a conservative approach be adopted and accumulation of REE in the environment be minimised. There is considerable prospect for research on REE behaviour in the environment in NZ.

4.1.6 Silver

The priority ranking model ranked Ag in SP 35th, TSP 100th, fish101st, RRP 117th, AP 124th, plants 144th and piggery 183th. Median concentrations in SP, TSP and in fish products were 1.74, 0.30 and 0.30 mg kg^{-1} respectively (Table 2.2, Taylor et al. 2014c). Thus the main fertiliser to consider with regard to environmental impacts from Ag is SP and other fertiliser contributions appear minimal at this time. Although Ag has not commonly been considered an environmentally important metal, like Cd or Hg, and it was surprising to see the levels in some fertilisers, it has become increasingly used as antimicrobials in consumer products (e.g. liquid soaps, sunscreens) and antibiotics in recent years (Lorenz et al. 2011), and there is even a laundry machine, the Samsung Corporation SilverCare Washing Machine (Figure 4.7), designed to release Ag ions twice during the laundry process (Jung et al. 2008). Both Ag ions and Ag nanoparticles have potential to disrupt basic metabolic functions and enzymatic resource acquisition (Gil-Allué et al. 2015), so the transfer of Ag to the wider environment requires attention. Ag nanoparticles are increasingly included in clothing, paints, food containers, automobiles, building materials and medical equipment (Evans & Barabash 2010). Ag is also used in animal supplements and remedies (Figure 4.8) and this is likely to increase the amount of Ag received by the wider environment in the future. Manures and other products derived from these sources for use as fertilisers may be elevated in Ag.

Other sources of Ag include emissions from smelting operations, the imaging industry, electronics, coal combustion and cloud seeding (WHO 2002, Purcell & Peters 1998). Long-range global transport of Ag occurs as atmospherically borne fine particles (WHO 2002).

Figure 4.7: Advertising for the Samsung Corporation SilverCare Washing Machine.

Ag has no known vital biological functions and is considered toxic, persistent and bioaccumulative to meso and microbiota (Kabata-Pendias & Mukherjee 2007). However, Ag

is not known as a systemic toxin to humans and other higher animals except at extreme doses, where compounds can be absorbed by body tissues causing consequent bluish or blackish skin pigmentation (argiria) or eyes (argyrosis). Other health effects include liver and kidney damage, irritation of the eyes, skin, respiratory and intestinal tract, and changes in blood cells (Drake & Hazelwood 2005). Mitigating the potential environmental and health risks are Ag ion's tendencies to form strong complexes in soil (e.g. with sulphides) that appear to be of very low bioavailability and toxicity (Luoma 2008). While insoluble forms of Ag appear to be of low environmental risk, studies demonstrate that some forms of Ag are more toxic than others (Drake & Hazelwood 2005) and soluble compounds may pose some hazard. Another consideration is that Ag becomes more mobile below pH 4 (Kabata-Pendias et al. 2001) and soil acidification could influence availability.

Silver Hydrosol Supplement

Figure 4.8: Some personal care products and animal remedies containing Ag (Silver Hydrosol).

Ecotoxicity tests and environmental case studies showed that Ag metal caused adverse effects to aquatic organisms at concentrations equal to or greater than 0.00005 g m^{-3} (Luoma 2008), while some embryonic and larval stages had thresholds as low as 0.000001 g m^{-3} (Ratte 1999). Trout development is affected at concentrations as low as 0.00017 g m^{-3}. Ag^{+} was lethal to representative species of sensitive aquatic plants, invertebrates, and teleosts at water

concentrations of 0.001–0.005 g m^{-3}. Ag nanoparticles disrupted basic metabolic functions and enzymatic resource acquisition of stream periphyton and adversely affect species composition and succession at 0.0003–0.0006 g m^{-3} (Gil-Allué et al. 2015, WHO 2002).

Terrestrial species can also be adversely affected by Ag. Earthworms had reduced growth in soil with 62 mg kg^{-1} Ag_2S, a relatively insoluble and less toxic Ag compound (Ewell et al. 1993, quoted in Kabata-Pendias & Mukherjee 2007). Nitrifying bacteria in the soil were inhibited at concentrations 540 - 2700 mg Ag kg^{-1} (Choi & Hu 2008). As Ag is so highly toxic to bacteria, it is used in medicine as a bactericide and a fungicide (Drake & Hazelwood 2005).

Plant tolerance of Ag varies widely but most plants tested showed no significant toxicity and growth reduction (Kabata-Pendias & Mukherjee 2007). However, some plants were sensitive to Ag, e.g. Ag was shown to cause ruptures to the rhizodermis in cowpea and these rhizotoxic effects are similar to those of Cu, Hg, Al, and La (Blamey et al. 2010, Kopittke et al. 2008). Wallace et al. (1977) reported that a nominal 100mM Ag was lethal to bean (Phaseolus vulgaris L.).

Most of the Ag applied to soil was expected to accumulate as it is only moderately mobile (K_d typically 250-300, Appendix 2.8), with a smaller proportion expected to transfer from soil as leachate or to be taken up by plants. Soils under kiwifruit had had the highest median concentration (0.27 mg kg^{-1}), similar to the European median for topsoil (0.25 mg kg^{-1}, Salminen et al. 2005), and significantly higher (at $P<0.05$) compared to soils under vegetable production, all pasture production land uses, production forestry and native land uses (Table 3.7). Vineyard soils also had similar Ag concentrations to kiwifruit (median 0.23 mg kg^{-1}), but there are only five sites, which makes assessment of statistical significance difficult. In comparison, soils under dairy and forestry land uses (median 0.08 and 0.06 mg kg^{-1}, respectively) had the lowest median concentrations, similar to the World BG of 0.09 mg kg^{-1} (Table 2.2).

The overall estimated application in SP in the top 10 cm of soil was 0.06 mg kg^{-1}, while the measured accumulation of Ag was 0.20 mg kg^{-1} (Table 3.8). Also, mixing by ploughing and soil organisms will increase the depth of soil impacted by Hg but dilute its concentration. It is apparent that fertiliser-Ag is about a third of the amount applied to soil in NZ.

The accumulation rate for Ag was estimated from the data in this thesis by dividing the difference between BG soil and the median concentration of all fertilised sites (0.20 mg kg^{-1}) by the estimated time fertiliser had been applied (65 y). This gave an accumulation rate of 0.0030 mg kg^{-1} y^{-1} from all sources.

The cause of the elevated Ag in soils under kiwifruit and vineyards is not clear, but fertilisers and pesticides are possible sources. Kiwifruit orchards are a high intensity crop so receive large P fertiliser inputs, e.g. applications of 1 t ha^{-1} SP or RRP + mixtures of "organic inputs" were recorded at some of these sites. Adding 1 t ha^{-1} SP would add about 1740 mg Ag ha^{-1}, which corresponds to an accumulation rate of 0.0022 mg kg^{-1} y^{-1}. The difference in concentrations between BG soils and kiwifruit is 0.18 mg kg^{-1}. Although fertiliser may account for nearly all the accumulated Ag in kiwifruit soils, more than 80 years of application at this rate would be required to account for the elevated Ag observed.

The large applications of environmentally sensitive trace elements to organically farmed kiwifruit may be of particular concern to organic kiwifruit growers. However, vineyards do not receive such large inputs of P fertilisers. Also, dairy farms also require considerable inputs of P fertilisers but Ag concentrations in these soils were not elevated.

Pest control is important in all forms of horticulture and arable cropping. However, no individual Ag pesticide product was identified, although Ag may be present as an ingredient or contaminant in existing products. Also, soils under vegetable production, which could be expected to receive similar pesticides to kiwifruit and vineyards, had significantly lower Ag concentrations compared to kiwifruit (median 0.12 mg kg^{-1}, $p=0.002$).

Sorption is the dominant process that controls the movement of Ag in soils. Ag adsorbs to Mn oxides, Fe compounds, organic matter and clay minerals (Jacobson et al. 2005a, WHO 2002), e.g. at pH 4-8, Ag is adsorbed onto Fe hydroxides (Lottermoser 1999). Ag-spiking experiments in Japan, on similar soils to those found in NZ, reported Ag correlated with organic matter, Al and allophane contents, and surface area; with most topsoil Ag in the residual and organic fractions (Hou et al. 2006, Hou et al. 2005, Jones et al. 1986).

In comparison, PCA of the soils data showed Ag to be associated with the first two components. Ag was mainly associated with component 2 (factor coordinate 0.542), which included Mn and explained 4.2% of the variance (Table 3.6). In addition, Ag was also associated with component 1 (factor coordinate 0.366), which included Al and Fe and explained 11.5 % of the variance. Spearman's rank correlation shows Ag to strongly correlate with Al (r=0.776), Fe (r=0.475) and Mn (r= 0.608), but much less so with C (r=0.198). Due to the large number of samples, all these correlations are significant at p=0.05. In NZ soils Ag appears to be sorbed mainly onto inorganic components.

Ag may leach from soils into groundwater in acidic conditions, the leaching rate increasing with decreasing pH and increasing drainage (ATSDR 1990, quoted in WHO 2002). Ag salts generally have low solubility at pH >4 (Jacobson et al 2005a). Under oxidising conditions, Ag forms strong multihalide complexes, while, under reducing conditions, Ag_2S predominates along with the free metal (Evans and Barabash 2010, ATSDR 1990, quoted in WHO 2002). The NZ soils set had pHs >4, so leaching is likely minor even though rainfall can quite high (1-3 m in the regions studied). At pH >6.5 Ag adsorbs into Fe oxides (Evans and Barabash 2010). Kiwifruit and vineyards have soil pH near 7 in NZ, whereas soil under dairy average 5.8 (Appendix 1.2).

Redox potential also can affect Ag mobility and the presence of DOC or thiol ligands may solubilise Ag, e.g. lower oxidation potentials can promote the formation of $S_2O_3^{2-}$, which can form soluble complexes with Ag (Jacobson et al. 2005a, b). The Ag thiosulphate complexes remain mobile until entering more oxidising conditions. Similarly, Ag can be mobilised

attached to DOC or fixed to SOM (Jones et al. 1986). However, redox effects in kiwifruit orchards and vineyards are unlikely as these plants do not grow in reducing conditions.

The reasons that Ag is elevated in soils under kiwifruit and vineyards have not been identified, although adsorption onto Fe oxides may play some role in retaining applied Ag. Although the amount of Ag actually applied to soil in the past was likely low, the increased use of Ag may lead to increased quantities in non-mineral fertiliser raw materials in the future. So, consideration should be given to understanding Ag's behaviour in the wider environment.

Concentrations measured in surface water were below the detection limit of 0.00005 g m^{-3}. Ag^{+} binds strongly with sulphide ions in inorganic and organic species, resulting in nanogram per litre aqueous dissolved concentrations (Bell & Kramer, 1999). In fresh water, the primary Ag compounds under oxidising conditions are bromides, chlorides, and iodides; under reducing conditions, AgS and the free metal predominate (ATSDR 1990, quoted by Salminen et al. 2005).

Median Ag concentrations in sediments from dune and riverine lakes, estuarine sediments from the west coast and northern Firth of Thames, Waikato region, and from the Wellington region were similar or lower to those in BG soil (Table 3.15). However, the median Ag concentration in peat lake sediments (0.17 mg kg^{-1}) was about twice that of NZ and world BG soils (0.08 mg kg^{-1}, Table 3.15 and 0.09 mg kg^{-1}, Table 2.2), while the median Ag concentration in estuarine sediments from the Appletree transect (0.84 mg kg^{-1}, Table 3.15) were an order of magnitude greater than the BG soils.

Ag adsorbs to Mn and Fe oxides, and clay minerals. Sorption by MnO_2 and precipitation with halides reduce the concentration of dissolved Ag, resulting in higher concentrations in sediments than in the water column (US EPA 1980). Ag strongly bound to S or precipitated as AgCl, in estuarine sediments was considered immobilised (Evans et al. 2010). However, in marine environments, Ag is strongly controlled by salinity, because of the affinity of Ag for Cl^{-} (Sanders and Abbe 1987). Ag also sorbs readily to phytoplankton and to suspended

sediments. However, sorption decreases as salinity increases, e.g. nearly 80% of Ag sorbed to suspended sediments at low salinities desorbs at higher salinities. However, desorption does not occur when Ag is associated with phytoplankton. Thus, Ag incorporation in or on cellular material increases its retention in estuaries and reduces Ag mobility (Sanders and Abbe 1987). It may be that Ag behaviour is much more complex than anticipated due to the dynamics of the brackish and estuarine environments.

Sediment resuspension is another mechanism that may transfer a significant quantity of solid phase sorbed trace elements to more bioavailable and mobile dissolved phases. Sediments can be resuspended in shallow lakes and estuaries due to currents, waves and wind action. Kalnejais et al (2010) reported 5–7% of the particulate Ag was released to the dissolved phase over 90h due to resuspention of coastal sediments.

Resuspended elements may then be taken up by biota or scavenged by other phases, such as by Fe oxyhydroxides (Kalnejais et al 2015). Adsorbed Ag in sediments may be released under reducing conditions and subsequently reduced to metallic Ag, or it may combine with reduced S to form the insoluble Ag_2S (US EPA 1980). So sediments may also be a both significant sink and source of Ag from and to the water column and the wider environment.

PCA of lake sediments showed Ag to be in same component as Al (Spearman Rank Correlation r = 0.85), suggesting lake sediment Ag is associated with clays. Ag is likely incorporated into the clay matrix as Ag in stream sediments was reported transported in the residual fraction (Lottermoser et al. 1999). Erosion and deposition of clay particles due to fluvial action is a well established mechanism for transfer of soil nutrient and contaminants (Walling and Collins 2008). PCA analysis of estuarine sediments also shows Ag to be in component 1 in association with Al (Spearman's rank correlation r=0.746). However, both Fe (0.404) and Mn (0.413) are also positively loaded on component 1 and have significant ($p<0.05$) correlations with Ag (Spearman's rank correlation r=0.704 and 0.675, respectively). These results could be explained by Fe and Mn coatings of clay minerals with resuspended Ag being scavenged by Fe and Mn oxides. The enhanced levels of Ag in estuarine sediments

suggest some of the applied Ag in soil may move, possibly by particles transfer, to the reduced estuarine environment where Ag reacts with Cl^-.

Even though SP may contribute to Ag accumulation in the environment, food-chain biomagnification of Ag in aquatic systems is unlikely at concentrations normally encountered (Connell et al. 1991, Ratte 1999). However, continuous inputs of low concentrations of Ag have been reported to result in changes in reduced growth, species composition and species succession (Sanders et al 1990).

Due to its potent antimicrobial action, Ag in the form of nanometer-size particles is one of the most promising nanomaterials currently in use but its toxicity on organisms and ecological systems remain poorly understood (Lara et al. 2011). Ag is increasingly used as a microcode and may increase in materials used for non-mineral fertilisers.

Results suggested little Ag has been applied to NZ soils thus far, while the enhanced levels of Ag in estuarine sediments suggest Ag may transfer from soil to estuaries. Therefore, a watching brief should be kept on this element by researchers to better identify transfer and accumulation mechanisms, as well as any environmental risks. Ag is not currently measured in NZ Regional Council surface water or groundwater monitoring samples. Such monitoring may be justified to guide regulations if these are required to minimise harmful impacts on humans and the environment.

4.1.7 Boron

The priority ranking model ranked B in RRP 10th, TSP 12th, blended 16th, SP 18th, AP 21st, poultry 55th, cattle 78th, piggery 83rd, plants 140th, and fish 168th (Table 3.5). All mineral fertilisers derived from P rock had F: BG ratios of >7 (Table 2.2, Taylor et al. 2014c), and may have sufficient B to cause significant environmental effects. B is an essential element for some algae, bacteria, fish and higher plants. It is possibly essential for yeast, animals (e.g. frogs and mice) and humans (Kot 2009, Hunt & Stoecker 1996). However, the average concentration of B in rocks is 10 mg kg^{-1} and many of the earth's soils contain <10 mg kg^{-1} B, while the critical soil value for avoiding deficiency is about 15-25 mg kg^{-1} (Woods 1994).

In comparison, the median world value for B from background sites is 29 mg kg^{-1}, while the median for only the NZ soils is 4 mg kg^{-1} (Appendix 2.2).). B has low retention in soil as it is predominantly present as undissociated boric acid at pH <8 (Schulin et al. 2010). B is thus mobile in humid climates and large areas of the world, including NZ, are B deficient.

However, there is a narrow range between deficiency and toxicity, and great variation in the requirement and tolerance of B by different plant species (Paull et al. 1988). Hence sensitive plants, such as citrus, cereals or cotton, may be affected even by low B concentrations in soil solution, e.g. 1 mg L^{-1} may affect sensitive plants, but 5 mg L^{-1} may be tolerated by many plant species, whereas 10 to 15 mg L^{-1} was shown to be toxic to tolerant plants (Salminen et al. 2005, Paull et al. 1988).

Although not as common as deficiency, B toxicity in soil decreases crop yields in some regions of the world (Nable et al. 1997), and has lead to investigations of the mechanisms involved in B toxicity tolerance (Schnurbush et al. 2010). Bacteria have acute and chronic effect concentrations between 8-340 mg L^{-1}, while protozoa are reported to be more sensitive (WHO 1998). Invertebrates are less sensitive to B than microorganisms. For several species, 24- to 48-h EC_{50} values ranged from 95-1376 mg L^{-1}. Also, high B concentrations (10-300 mg L^{-1}) in water may be toxic to fish and other aquatic species (Gowariker et al. 2009). Rainbow trout, an important game fish in NZ, was the most sensitive fish species reported by WHO (1998) with NOECs ranging from 0.009-0.103 mg L^{-1}.

B is naturally present in RRP (Table 2.2) and high median B concentrations were found in all fertilisers derived from P rock (130-500 mg kg^{-1}, Appendix 2.3), up to 17 times the guideline values of 29 mg kg^{-1} (MfE 2013) for soil organisms and plants.

As well as the component in P rock, B can also be deliberately added to fertilisers or applied directly as foliar applications to plants to overcome deficiency (Magda et al. 2010). B is also widely used in industry for the production of commercial materials such as insulation, glass fibres, bleaches, borosilicate glass, herbicides and insecticides (Schnurbush et al. 2010) and as powder coatings to prevent corrosion and oxidation (Petrova et al. 2007). However, the size of

these industries in NZ is small compared to Europe and the contribution of B to the NZ environment from these sources is likely minor. In NZ, geothermal discharges of B, along with As, Cs and Li also contribute to loads in surface waters. These discharges are from natural geothermal activity and from power generation.

B was predicted to be very mobile (K_d typically 40-60, Appendix 2.8), easily taken up by plants (TF typically 15-35, Appendix 2.9). Consistent with this prediction, Tables 3.7 showed B to be significantly depleted in NZ soils under fertilised land uses assessed in this study despite the applications of B in fertiliser and from other sources, except for kiwifruit production, which had significant accumulation. This is surprising as kiwifruit is a B sensitive crop. Excessive B reduces fruit yield and also is associated with premature ripening in cool storage (Smith et al. 1985).

The overall estimated application of B in the top 10 cm of soil was 5.79 mg kg^{-1}, while the measured average accumulation of B as SP was 0.80 mg kg^{-1} (Table 3.8). On an annual basis, an annual application of 71 kg B ha^{-1} would be applied. While mixing by ploughing and soil organisms will have increased the depth of soil impacted by B and dilute its measured concentration, mixing cannot account for all the B applied. Thus, a large amount of the B applied in fertilisers was not accounted for.

Although kiwifruit is a high intensity crop, thus receives high P fertiliser inputs (Appendix 1.2), B in irrigation water, pesticides or leached from treated timber may have added to total B inputs. Both river and ground waters may be used for irrigation of kiwifruit. B was elevated in water from dune and riverine lakes and the Waikato River compared to streams and rivers from the Wellington region (Table 3.10), while the median in groundwater in the Waikato region was 0.02 mg L^{-1}. Boric acid is commonly used as a timber preservative in NZ (Robinson et al. 2007), so B may leach into the soil if the kiwifruit vines are grown over timber framing.

Soil texture, pH, SOM and the soil moisture content affect the movement of B in soils. Coarse textured sandy soils poorly adsorb B and are often deficient. Fine-textured soils are more able

to retain added B on a variety of clay minerals (Gowariker et al. 2009, Parks & Edwards 2005) with maximum adsorption at pH 8-10 (Kot 2009). However, none of the soils in this study had pH above 7.5 (Appendix 1.2). Soil pH is one of the most important factors affecting B mobility as relatively little boron adsorption on the mineral fraction occurs at low pH levels (Gu & Lowe 1990). Organic matter is one of the controllers of boron in acid soils, although B adsorption on soil humic acid also increases with increasing pH, up to a maximum near pH 9.5 (Salminen et al. 2005).

NZ soils generally have high organic matter content (Appendix 1.2) but B has depleted despite considerable B applied in fertiliser and other possible sources. Adsorbed B on soil minerals is temporary and easily mobilised (Nable et al. 1997), while B associated with SOM can be mobilised by microbial action (Parks & Edwards 2005). In addition, competition effects from phosphate ions depress the absorption of B (Kot 2009), while Ca seems to increase adsorption, e.g. excessive liming of soil can induce B deficiency or reduce toxicity (Gowariker et al. 2009, Maier et al. 2002, Dwivedi et al. 1992).

Highly soluble B follows the water flux and it is not redox-sensitive under typical environmental conditions. So B has a high potential to be leached downward in soil profiles by drainage water as boric acid [$B(OH)_3$] (Kot 2009, Komor 1997), e.g. Chang & Page (2000) estimated B depletion from soil to subsurface drainage to be between 18-24 kg ha^{-1} in the San Joaquin Valley, USA. Thus, B is likely to be transferred to groundwater aquifers and from groundwater springs to surface water, especially in temperate climates, e.g. agriculturally derived B contributed about 10% of the B discharge to the highly urbanised Seine River, France, (Chetelat & Gaillardet 2005). Concern about movement of B into drinking water sources in the USA has lead the US Environmental Protection Agency to consider regulating it in drinking water (Parks & Edwards 2005).

In NZ, the B trigger value for freshwater protection for 95% of species is 0.37 g m^{-3}, (ANZECC 2000) and median water concentrations were all below this (Table 3.10). The 95% protection level is the slightly impacted level, indicating B concentrations are generally having minimal impact on aquatic ecological receptors. Some individual lakes and streams

exceeded this 95% protection level at times, e.g. Lake Waahi had B concentrations as high as 0.92 g m^{-3} (Table 3.11). As discussed in section 4.1.3, the high concentrations in this lake concentrations were attributed to water pH change to >8.5 due to algal blooms. However, these concentrations were well below the trigger value for freshwater protection for 80% of species, which is 1.3 g m^{-3}, (ANZECC 2000).

PCA of Waikato lake waters showed B to be highly loaded on component 1, along with Ca, Mg and Na, as well as Mo, Sr, and U, while PCA of the Waikato River water showed B to be highly negatively loaded on component 4, along with Na and Sr. This is interpreted as elements existing as free ions in the water, unattached to clays, Al, Fe, Mn or organic matter.

Although fertilised soils were depleted in B and B was elevated in some lakes and the Waikato River, B did not accumulate appreciably in lake sediment. Dune and peat lake sediments had median B concentrations similar to those for background soil in NZ (Table 3.15), while riverine lake sediment was about two times higher. In comparison, B concentrations in estuarine sediments were higher still. Samples from Appletree, Firth of Thames, had the highest B concentrations, 15 times the background soil level, while sediments from other estuaries in the Waikato region had B concentrations 3-6 times the background soil level. B was not analysed in the sediments from estuaries outside the Waikato region. These results are consistent with the established view that B is incorporated into fine-grained sediments once it reaches the marine environment (Boon & MacIntyre 1968, Liss & Pointon 1973). Appletree receives discharge from the Piako River, which is has one of the most intensively farmed catchments in the Waikato Region, and little known geothermal activity. Thus, the high levels of B found at this site are likely to have come from agricultural sources.

Mance et al. (1988) and Grimwood and Dixon (1997) reviewed the toxicity of B to saltwater organisms. They found only limited data, which made it difficult to determine whether any group of organisms exhibited greater sensitivity. There remains a need to establish the ecotoxicity of B to marine organisms.

The chemical behaviour of B in the brackish environment, at the meeting of fresh and salt waters, also appears little studied. This ecosystem may be important in the accumulation of B in estuarine sediments compared with lake sediments and soils. The lack of information of B (and other elements) in the brackish ecosystem may limit effective management of this resource. The change from a low B estuarine environment to one where B is abundant or even toxic has considerable implications for the aquiculture industry. Consideration should be given to identifying and quantifying the source of B accumulation in the estuarine environment so that suitable controls can be developed.

4.1.8 Molybdenum

The priority ranking model ranked Mo in RRP 38th, TSP 39th, piggery 50th, poultry 51st, AP 52nd, SP 62nd, blended 65th, cattle 69th and fish 112th (Table 3.5). Mo was expected to be very mobile (K_d typically 75-240, Appendix 2.8), while high median Mo concentrations (Table 2.2, Taylor et al. 2014c) were found in TSP (5.5 mg kg^{-1}) , RRP (5.7 mg kg^{-1}) and poultry products (3.6 mg kg^{-1}), up to 2½ times soil guideline values (plants 2 mg/kg, Appendix 2.11). Due to its high mobility, it was not expected to accumulate in the soil.

Mo is considered essential for plants, mammals, some microorganisms and aquatic organisms, but Mo requirement is relatively low and it may become toxic at high concentrations to plants, microorganisms (Kabata-Pendias & Murkherjee 2007, Chang & Page 2000) and to animals, even at quite low concentrations (Gowariker et al. 2009). Acidic soils, especially sands, such as are found in New Zealand, are generally Mo deficient (Gowariker et al. 2009), e.g.108 samples analysed by XRF had a median of 2.2 mg kg^{-1} (Appendix 1.2), compared to the critical limits to avoid plant deficiency of 2-13 mg kg^{-1} (Schulin et al. 2010). Rhizobium bacteria and other N-fixing microorganisms have an especially large requirement for Mo. Thus Mo deficiency may be an issue for NZ clover/ryegrass based pastoral system.

Sources of Mo, other than fertiliser applications, tend to be urban based and include the steel industry, oils, burning fossil fuels, ceramic and sewage sludge (Salminen et al. 2005).

Table 3.7 shows that Mo levels in soils under vineyards and production forestry displayed significant depletion compared to other land uses, while Mo accumulated significantly in NZ soils only under intensive vegetable production. All other land uses showed Mo levels in soil not significantly different from soils under native land use. Soils under intensive vegetable production, generally, had pH nearer neutral than soils under pasture (average 6.3 and 5.9 respectively) and a lower SOM content (average total C 3.3% and 7.5% respectively) and Mo is more mobile under these conditions. So, for this land use group to be the only one showing significant accumulation is surprising. It is suggested that, due to the known deficiency of Mo in NZ soils, vegetable growers are likely directly applying Mo fertiliser.

The overall estimated application of Mo in SP in the top 10 cm of soil was 0.10 mg kg^{-1}, while the measured average accumulation of Mo was 0.50 mg kg^{-1} (Table 3.8). On an annual basis, an annual application of 1.2 kg Mo ha^{-1} would be applied. While mixing by ploughing and soil organisms will increase the depth of soil impacted by Mo and dilute its measured concentration, mixing cannot account for the entire Mo applied. Thus, about 80% of the Mo applied in fertilisers is not accounted for in the soil.

Vegetables produced on the Mo-elevated soils are for human consumption and, while Mo toxicity in plants under field conditions is rare, toxicities to animals feeding on plants high in this element are well-known. Mo may be very toxic to animals, even at quite low concentrations. Mo interacts with several other elements including P, S, Zn, Fe and, most importantly, with Cu (Gowariker et al. 2009). Soil factors that increase the availability of Mo to plants usually have inhibitory effects on Cu uptake. Nutritional effects of Cu/Mo ratios in pastures on animal health are controlled by the sulphate concentration in plants, e.g. increased sulphate ion concentrations in the plant can result in reduced Cu absorption, even with low concentrations of Mo (Kabata-Pendias & Pendias 2001). Excess Mo can cause Cu deficiency at otherwise sufficient Cu levels (molybdenosis), whereas poisoning may occur at relatively moderate Cu levels if the Mo intake is too low (Steinnes 2009). Molybdenosis is caused by imbalance of Cu and Mo in the diet and this ratio also affects the metabolism of S. If plants are consistently low in Mo content, vegetarians may be at increased risk of molybdenosis (Steinnes 2009).

The depletion of Mo under vineyard soil and production forestry (Table 3.7) may be due to leaching of Mo. These land uses tend to occur on stony or otherwise "poor quality" soils that can have low anion retention capacities. P competes strongly with Mo for the limited sorption sites and will tend to push Mo into soil pore water, where it can be taken up by plants or leached to groundwater (Vistoso et al. 2012). Another factor for vineyards is that vineyard soils had low SOM content for NZ soils (average total C 4.3%) and near neutral soil pH (average 6.4), which favoured Mo mobility. In addition, the abundance of stones >7% of the bulk soil for vineyard soils may cause greater leaching by increasing by-pass flow (Lilburne & Webb 2002) and Mo taken up in plant foliage may be lost from the farming system if prunings are removed from the vineyard.

The mobility of Mo is difficult to predict due to adsoption and coprecipitation reactions being highly dependent on pH and Eh conditions (Salminen et al. 2005). Solubility and availability of Mo to plants is largely controlled by soil pH and drainage conditions. Mo behaviour in soils differs from that of most other trace metals as its availability increases from slightly mobile in acid soils (pH <4–5) to readily mobilised in neutral to alkaline soils (pH >6.5) with the MoO_4^{2-} anion dominating in neutral and moderately alkaline soils and $HMoO_4^-$ in acid soils (Kabata-Pendias & Murkherjee 2007). Under acidic conditions (pH <5), Mo is reported to be retained by soils on the surfaces of variable-charge minerals, such as the Fe oxides but sorption decreases rapidly as pH increases to 8 (Evens and Barabash. 2010). Mo may also be sorbed by SOM, complexed with carboxylic and phenol groups.

The increased mobility of Mo as pH increases may be a concern where there are several metals present at toxic concentrations as increasing soil pH is one of the most common and practice ways of reducing the bioavailability of M^{2+} cations.

Wet (i.e. reducing), alkaline soils favour Mo availability (Salminen et al. 2005). These conditions are uncommon in NZ but do occur in many other countries with limited rainfall, e.g. Parts of the USA, Australia, Argentina, Egypt and other North African countries. Under reducing conditions Mo is usually associated with sulphur, but under other environmental

conditions it is likely to form oxyanions (Schulin et al. 2010). Conversely, Mo is poorly available to plants on acid soils (pH <5.5), and especially on those with high concentrations of iron oxides (Kabata-Pendias & Murkherjee 2007). In peat soils, humic acid may strongly fix Mo ions, resulting in low availability. Conversely, in organic-rich soils, slow release of Mo from the decay of SOM can supply adequate amounts of Mo.

There were no measurements of Mo in groundwater. River and lake water had low Mo concentrations near the detection limit, while PCA showed Mo highly loaded on the same components as U for both river and lake water, suggesting a common source (Tables 3.10, 13). Consideration should be given to investigating the behaviour of Mo in waters under different land uses as there appears to be considerable potential for Mo to leach from fertiliser applications to NZ soils.

No consistent patterns in Mo concentration were seen in sediments (Table 3.15) so these are unlikely to act as a sink for Mo and Mo is not accumulating in these sediments. PCA and correlation analysis suggests Mo is associated with several major controlling elements, including OC, Al and Ca in lake sediments (Tables 3.16-17), and OC, Al, Fe, and Mn in estuarine sediments (Tables 3.18-19). Of these, ferromanganese oxides in sediments are reported to accumulation large amounts of Mo (Kabata-Pendias & Murkherjee 2007).

Overall, the fate of Mo derived from P fertilisers is somewhat unknown and there are significant information gaps that could be further investigated. These include identifying if Mo inputs are sufficient for healthy production, if significant losses through leaching are occurring and, if so, identifying the ultimate sink and any associated environmental impacts.

4.1.10 Chromium

Cr in RRP was ranked 31st, AP 36th, TSP 42nd, SP 85th, Blended 87th, plants 104th, poultry 104th, piggery 128th and fish 187th by the ranking model (Table 3.5). However, only moderate concentrations were found in RRP, AP and TSP fertilisers (114, 102 and 83 mg kg^{-1}, respectively), about 2-2.5 times soil BG values (42 mg kg^{-1}, Table 2.2). Stacey at al. (2010) described Cr as among the most common contaminant metals found in phosphate rock. Other

mineral and organic P fertilisers had Cr contents less than soil BG values. PCA of fertilisers showed Cr to be associated with P and in the same component as P, Cd, U and Ca (Table 3.1).

Cr is essential for animals and needed by the human body in small amounts for insulin action and the metabolism of proteins and carbohydrates but it has a varying toxicity depending on its valency and speciation in the environment, with Cr(VI) being much more toxic than Cr(III) (Ma & Hooda 2010, Salminen et al. 2005). Soluble Cr^{3+} is considered relatively harmless at levels normally encountered, but Cr^{6+} is highly toxic because it bears a structural similarity to S(VI), causing liver and kidney damage and acting as a carcinogen (Ma & Hooda 2010, Salminen et al. 2005).

Large amounts of Cr are released to the atmosphere by human activity, e.g. from ferrochrome production and emissions associated with vehicles (McGrath 1995, Ward et al. 1977). However, source of these emissions in NZ are few and the reported average atmospheric Cr deposition flux for NZ is 2.8 mg m^{-2} y^{-1} (Gray et al 2003). Cr is also extensively used as a timber preservative in NZ (Carey et al. 1996) and soils surrounding treated timber have significantly higher Cr concentrations than control soils (Robinson et al. 2006). The deposited Cr is subject to adsorption or precipitation reactions, uptake by plants, and, under favourable soil pH and moisture conditions, leaching to subsurface layers.

Cr was predicted to be mobile (K_d typically 36, Appendix 2.8) but not readily taken up by plants (TF typically 0.0018, Appendix 2.9). Consistent with this prediction, measured depletion of Cr was 1.80 mg kg^{-1}, but the estimated application of Cr in superphosphate over 65 years was 0.97 mg kg^{-1}, about 11.9 kg ha^{-1} (Table 3.8). In addition, Table 3.7 showed despite considerable amounts of Cr being applied to soil in NZ in fertiliser and from other sources, Cr is not accumulating. Also, no land use differed significantly in Cr concentration from land under native plants.

PCA of the soils data showed Cr to be associated with Fe, Ni and V (Table 3.6). Similar strong correlation between Cr and Ni was reported in Salminen et al. (2005) (r = 0.89 in subsoil and 0.83 in topsoil). Ma and Hooda (2010) reported lithogenic Cr was generally associated with Fe,

while anthropogenic Cr was generally associated with OC. This suggests the Cr in soil is from natural weathering and Cr applied from anthropogenic sources, like fertilisers, is lost, probably in leaching.

In soil, Cr behaviour is governed by pH, Eh, Fe and Mn oxides, and organic matter. Organic matter stimulates the reduction of Cr^{6+} to Cr^{3+} (McGrath 1995). NZ soils tend to be slightly acidic and so applied Cr is expected to remain as Cr (III). Cr(III) is nearly immobile when bound to soil by adsorption or precipitation, especially under moderately oxidising and reducing conditions and near-neutral pH values (Ma & Hooda 2010, Salminen et al. 2005). This limits Cr entry into the food chain and leaching to groundwater. There also appears to be element-specific chemical barriers that limited the plant transfer of some potentially toxic elements from soil to plants, including Cr, e.g. Cr exhibits a low potential for plant absorption compared with Cd, Cu, Ni, and Zn under the same conditions (Chen et al. 2010). Thus removal in product appears an unlikely loss mechanism.

However, the soils data presented above implied Cr is generally leaching in NZ soils. Under certain soil conditions, such as a neutral to alkaline pH accompanied by high soil manganese, significant oxidation and remobilisation of Cr can occur (Bartlett & James 1979). Farmed soils in NZ receive lime to bring the soil pH nearer to neutral. Also rainfall is plentiful in NZ and limited mobilisation and precipitation of Fe and Mn is common in some soils (Section 1.4, Figure 1.7). This may include soil microclimates where there is a low level equilibrium with a small proportion of Cr as Cr(VI). Compexation agents, such as citric acid, diethylenetriaminepentaacetic acid (DTPA), fulvic acids, and DOC are reported to keep Cr(III) in solution above pH 5.5, and prevented its immediate removal by soil (James & Bartlett 1983a). The process may be facilitation of Cr(III) oxidation by chelation and of further chelation by oxidation resulting in the continuous formation of Cr(VI) in soil (James & Bartlett 1983b). The Cr(VI) could leach down the soil profile until it was reduced to Cr(III) again.This could result in Cr moving below the depth of soil samples taken for theis study (10 cm), but not reaching groundwater.

Formation of CrF_x species as an analogue of aluminofluoride species could also be possible. F extracts soil Al and also changes the solution speciation from hydroxide to fluoride (Taylor and Kim 2009). F could also similarly increase Cr availability as adsorption and solubility behaviour of Cr(III) is similar to that of Al and NaF extracts organically bound Cr(III) (Bartlett & Kimble 1976).

As under neutral to alkaline soil pH conditions, Cr(VI) can be highly mobile, raising the pH as a standard procedure for reducing the risk of excessive plant uptake or leaching of contaminant metals may enhance bioavailability and leaching of Cr.

Despite the depletion seen in soils, Cr was below or at the detection limit when measured in surface and groundwater samples (Tables 3.10, 21). Although Cr was at concentrations at or below the detection limit, due to the plentiful rainfall, the flow of ground and surface waters can be considerable. Assuming 1000mm of drainage per annum, which will give 10,000 m^3 y^{-1} of drainage and a Cr concentration of 0.5 mg m^{-3}, only 5 g ha^{-1} y^{-1} of Cr can be accounted for in leaching and this mass of Cr would include natural Cr, the atmospheric deposition flux, as well as anthropogenic Cr. Thus, only a small proportion of the Cr unaccounted for in soils is likely leaching to water.

Cr was higher in dune lakes and in estuarine sediments from Waihou, Piako and Appletree and the Tasman region, compared with lake and estuarine sediments from other areas. However, these enrichments may be lithogenic as PCA of lake and estuarine sediments show Cr to be associated with Fe (Spearman's rank correlation r = 0.59 and 0.71, respectively, Ma and Hooda 2010). Concentrations of Cr at other sites were similar to BG soils. Also, Ultramafic soils from the Tasman Region have been reported to contain high total levels of Cr as well as Co, Fe, Mg, Mn and Ni (Robinson et al 1996). These results are consistent with Cr moving in soil particles during erosion and deposition events. However, this would not deplete soils as the whole soil particle is transported.

Despite several known sources of Cr to soil in NZ (the atmospheric deposition flux, fertilisers, treated timber), it is on average depleting in the top 10 cm of soil and elevated concentrations can

be found in some lake and estuarine sediments. Movement as dissolved Cr appears minimal and another mechanism, such as particle transfer, must be responsible for transfer of Cr to sediment.

4.1.11 Selenium

The priority ranking model ranked Se in RRP 48th, fish 49th, SP 54th, AP 68th, poultry 70th, piggery 72nd, blended 74th and cattle 91st (Table 3.5). Median concentrations of Se in fertilisers are relatively low (0.6 – 2.7 mg kg^{-1}, Table 2.2, Taylor et al. 2014c) compared to many other trace contaminants found in fertilisers. Higher median concentrations of Se were found in fertilisers derived from fish products (2.5 mg kg^{-1}) and from P rock, e.g. TSP 2.7 mg kg^{-1}.

Se is an essential element for humans and many other animals but is not essential for plants (He et al. 2010). However, the optimal Se intake lies within a narrow range and it is toxic at high concentrations, but Se toxicity generally only occurs in alkali soils of arid and semiarid areas (He et al. 2010). As Se is also bioaccumulative, both deficiency and toxicity problems are found around the world (Santos et al. 2015, Salminen et al. 2005). Se is also of environmental concern due to its ability to bioaccumulate rapidly, particularly in the aquatic environment (Lemly 2004).

Se concentrations in NZ volcanic soils are often low as Se escapes with high-temperature volcanic gases during eruptions (Hartikainen 2005, Salminen et al. 2005). In comparison, soils containing naturally high concentrations of Se are typically associated with sedimentary phosphate rocks (up to 300 mg kg^{-1}), organic-rich black shales, coals, and sulphide mineralisation (Vodyanitskii 2010, Fordyce 2007). So it was not surprising that high median Se concentrations (Table 2.2) were found in fertilisers derived from phosphate rock (TSP 2.7 mg kg^{-1}, RRP 2.5 mg kg^{-1}). These were nearly 3 times soil guideline values for plant and human health of 1 mg kg^{-1}, Appendix 2.11). However, concentrations in fertilisers from fish products (2.5 mg kg^{-1}), were similarly elevated in Se, possibly due to bioaccumulation from seawater.

Sources of Se other than fertilisers include mining, fossil fuel combustion, especially coal, and oil refining (Santos et al. 2015, He et al. 2010).

Concentrations of Se in NZ soils were generally below the detection limit (2 mg kg^{-1}) available for Se from commercial laboratories in NZ, and there were too few measurements to carry out statistical analysis of its behaviour under different land uses (Table 3.7). He et al. (2010) reported a mean value of 0.2 mg kg^{-1} for agricultural soils with a range of 0.1-2.0 mg kg^{-1}.

However, simply comparing all fertilised samples with the unfertilised ones indicated no accumulation of Se at fertilised sites compared to non fertilised sites (Figure 3.4). Thus, applications of Se in fertilisers are not accumulating in NZ soils and these are likely beneficial to higher organisms in NZ.

The overall estimated application of Se in SP in the top 10 cm of soil was 0.07 mg kg^{-1}, while the measured accumulation of Se was 0.03 mg kg^{-1} (Table 3.8). While mixing by ploughing and soil organisms will increase the depth of soil impacted by Se and dilute its measured concentration, mixing is unlikely to account for the entire Se applied. Thus, some of the Se applied in fertilisers is not accounted for. However, amounts are small. On an annual basis, an annual application of 0.9 kg Se ha^{-1} would be applied.

Temperature, rainfall and soil hydrological conditions are important in the transformation, availability, and mobility of Se. The temperate humid climate in NZ results in moist but oxidised soil conditions, similar to the low-Se belt of China (He et al. 2010). Thus, Se was predicted to be highly mobile (K_d typically 20-125, Appendix 2.8) in NZ soils with the oxidized form of Se considered the most mobile, although it is slightly less mobile with increasing pH, while Se is relatively immobile under reducing conditions (Salminen et al. 2005). In fertilised soils, competition with phosphate and sulphate enhances both Se uptake and leaching (He et al. 2010).

The effects of organic matter on the availability and mobility of Se is somewhat complicated. Firstly, organic matter, particularly freshly added, can enhance the development of reducing conditions under flooding, as in paddy soils, thus affecting the transformation of Se. Secondly, humic substances, especially humate, can retain Se on their negatively charged functional groups such as R–COO-, R–O–, thus reducing its movement, whereas humic acids and fulvic acids can compete for adsorbing sites with selenite or selenate, thus increasing the availability of Se to plant.

Concentrations of Se in surface waters were also generally below the detection limit (<0.005).

As was expected, dune and riverine lake sediments, and estuarine sediments also had Se concentrations below the detection limit, while most peat lake sediments had Se concentrations just above the detection limit (Tables 3.15). The higher concentrations of Se in the peat lakes may be due to Se moving with DOM. An interesting comparison can be made with studies in Finland. Addition of fertilisers containing Se in Finland 1983-1992 resulted in increased Se in the river environment, especially bottom sediments (Kabata-Pendias, 2001). Large parts of Finland are dominated by Podzols and peat land soils and Se fixation to SOM is rapid in these acidic soils (Gustafsson & Johnsson, 1992). However, part of the SOM is mobile DOM, which can transport Se to rivers. A similar mechanism is likely in NZ.

Se is not currently measured in NZ Regional Council groundwater monitoring samples.

The current analysis testing is insufficient for protecting environmental health. This is because soils with Se concentrations less than 0.6 mg kg^{-1} are generally thought to produce crops with insufficient Se contents (<0.1 mg kg^{-1} feed) (Lenz & Lens 2009) to supply animals with adequate levels to protect them from deficiency (Gupta & Gupta, 2002). On the other hand, soils can also contain toxic levels of Se if in excess of 2 mg kg^{-1} (Gupta & Gupta 2000, Fordyce 2007), so it is important to monitor Se levels carefully in both directions. The commercial laboratory detection limit for Se in soil and sediment in NZ is 2 mg kg^{-1}, so there is a need for a better analysis method to be available for environmental management.

4.1.12 Tellurium

There is scarce data on Te in soils and in fertilisers. Median Te concentrations in European soils were reported to be 0.03mg kg^{-1} (Salminen et al. 2005) and correlated with Fe and Mn. In comparison, the background soils median value was 1 mg kg^{-1} (Table 2.2).Te measurements were only available for a few AP, BF and fertilisers derived from cattle products (Table 2.2). Therefore, this assessment should be used with caution. Te in fertilisers derived from cattle products (3.47 mg kg^{-1}) appeared elevated compared to background soil concentrations. However, the median concentrations in BF and AP was much lower (<0.003 mg kg^{-1}). The priority ranking model ranked Te in fertilisers made from cattle products 37^{th}, BF 188^{th}, and AP 199^{th} (Table 3.5). However, cattle appear to live normal lives so this level of Te may not be harmful or in a form that is harmful. Due to the limited data, this level could also only reflect a localised enrichment.

Te is not generally reported to have any biological function but may interact with Se. It is slightly radioactive as ^{128}Te and ^{130}Te have half-lives of 2.2×10^{24} years and 7.9×10^{20} years. However, Te is not usually considered to be of concern to the environment because of its rarity and the very-long-lived radioisotopes means practical exposure to a decay is unlikely during a human lifetime. Te is used in medicine as Tellurite has antibiotic properties due to the close chemical relationship between Te and S, while CdTe nanoparticles are fluorescent and can be used as quantum dots in imaging and diagnosis (Ba et al. 2010).

Although median world Te concentrations in soil were 1.0 mg kg^{-1} (Table 2.2), Ba et al. (2010) reported a global average of only 0.027 mg kg^{-1} and noted distribution of Te varies widely. There were Te data from XRF analysis for only 346 sites in the Waikato region. Median total Te was 2.0 mg kg^{-1} in fertilised soils and 1.7 mg kg^{-1} in background soils.

Te was predicted to be moderately mobile (K_d typically 300, Appendix 2.8), but not easily taken up by plants (TF typically 0.2, Appendix 2.9). The estimated application of Te in SP in the top 100 mm of soil was minimal, while the measured accumulation of Te was 0.35 mg kg^{-1} (Table 3.8). Thus, the fertiliser-Te contribution has been minor compared with concentrations already in soil. Also, other sources of Te make a far larger contribution. Consistent with fertiliser not being

a significant source of Te in NZ, there were no significant differences in Te concentrations in soil with land use (Table 3.7).

Te is particularly sensitive to soil redox conditions and the mobility of Te is reported to increase with the oxidation state (Vodyanitskii 2010). It is likely the redox conditions affected the Te transfer from soil to crops with soil:plant transfer factors for Te showed higher correlation for upland field crops (r = 0.577, p < 0.001), but no correlation found for brown rice (Yang et al 2014). Te has a high affinity for Fe oxides (Vodyanitskii 2010) and it is likely that Te is scavenged by Fe and Mn oxyhydroxides, although Te can also abiotically be methylated, which may increase its mobility in the aquatic environment.

Te is not monitored by regional councils in surface or ground waters, nor in sediment. In one study, dissolved Te in water was low owing to its low abundance in the Earth's crust, high insolubility in water, and strong affinity to particulate matter (Wu et al. 2014). Due to the limited data on Te, it should be treated with caution by resource managers, but levels found in NZ soils appear unlikely to be significantly harmful.

4.1.13 Zirconium

Zr in RRP was ranked 22nd by the ranking model, while Zr in other mineral P fertilisers were ranked >120. There was no information of Zr contents in the fertiliser groups from organic materials (Table 2.2, Taylor et al. 2014c) Only moderate concentrations were found in RRP fertilisers (790 mg kg^{-1}), about 3 times soil BG values (234 mg kg^{-1}, Table 2.2). Other mineral P fertilisers had median Zr contents less than soil BG values. This was despite observation of Zr being present in appreciable amount in inorganic fertiliser samples analysed by Senessi et al. (1988).

Zr is a nonessential element that has both stable and anthropogenic radioactive isotopes. It does not have any known essential function in plant or animal metabolism, but it can be taken up by plants (Salminen et al. 2005). However, there appears very limited information on the mechanisms of plant uptake, phytotoxicity and potential health risks (Shahid et al. 2013, Salminen et al. 2005). There is also scarce information on Zr toxicity but the stable isotopes

of Zr are considered to have low toxicity to biota (Shahid et al. 2013). There also appears to still be considerable scientific debate if Zr is mobile or not in soil (Shahid et al. 2013, Oliva et al. 1999).

Sources of Zr in NZ, other than fertiliser, are probably limited to a small quantity used in the chemical and ceramic industries as NZ has little heavy industry and does not have a nuclear power industry. Environmental concentrations of Zr in the northern hemisphere have increased due to increased use of Zr in industry and the Chernobyl and Fukashimia accidents (Shahid et al. 2013), but a similar increase has not been noted in NZ. Zr was predicted to accumulate in soils (K_d typically 500-1300, Appendix 2.8) and the proportion taken up by plants or transferred to water was predicted to be low (Typical plant TF 0.02-0.04, Appendix 2.9).

Some sites had been analysed by XRF but there was much less Zr data for soils under different land uses than for other elements (Table 3.7) and total Zr was not significantly different from native land use (217 mg kg^{-1}) for any land use. The estimated application of Zr as SP was 0.54 mg kg^{-1}, which is inconsequential compared to the levels found in the top 10 cm of soil in NZ (229 mg kg^{-1}, BG soils). However, total Zr concentrations were considerably higher in soil under vegetable production (385 mg kg^{-1}). Closer inspection of these sites showed the vast majority of measurements were on sites derived from basaltic ash and not receiving RRP (the only fertiliser measured with elevated concentrations of Zr, Table 2.2). That these higher concentrations were natural was confirmed by comparing with two background sites in native bush also derived from basalt (360 and 490 mg kg^{-1}, Appendix 1.2).

Zr has been considered so immobile that it is used as a resistant indicator and reference element in pedological and weathering process studies (Oliva et al. 1999, Sudom & St. Arnaud 1971) as it is mainly present as zircon grains in the coarse fraction of soils (Stiles et al. 2003). Even the weathering components are considered relatively immobile as Zr has low solubility, forms strong complexes with soil components and it has a strong tenancy to polymerise (Salminen et al. 2005), e.g. Zr was associated with Fe oxides (Riedel et al. 2015).

In addition, Ferrand et al. (2006) showed organic matter had a high affinity for added Zr, while Oliva et al. (1999) reported relatively high Zr concentrations in organic-rich soils.

However, some researchers have shown Zr to be redistributed within the weathered soil profile, with the mobility and loss of Zr increasing with mean annual precipitation (Kurtz et al. 2000). This redistribution appears likely to involve interactions with SOM. Oliva et al. (1999) suggested that organic acids enhance dissolution of Zr containing minerals such as zircon and these organic acids can then form mobile complexes. Transport by organic acids has also been suggested as the main transport mechanism for Zr by Kabata-Pendias & Pendias (2001), while Salminen et al. (2005) reported distributions of Zr in European stream water closely followed the REEs pattern, which were strongly controlled by DOC. Riedel et al. (2015) observed a release of metals typically bound to Fe and Mn oxides under oxic conditions, including Zr, during elution of biochar amended soil under anoxic conditions. They also observed the retention of DOM in the amended soil with the retention of DOM-associated elements.

Soil pH also appears to have a role in the partitioning of Zr between soil and soil solution as solubility increases as pH increases due to the formation of zirconate ions (Shahid et al. 2013)

Zr was not usually analysed as part of NZ regional council monitoring and it was not measured in lake or estuarine sediments, or in river or ground water. The limited literature available suggests texture appears to have a role in the deposition of Zr in sediments. Zr concentrations in active stream sediments are reported to be much higher than concentrations in soils due to deposition of heavy minerals. However, in lower energy environments, such as flood plains where clay and silt can deposit, concentrations of Zr were much less and similar to those found in soils (Salminen et al. 2005). So where lighter particles can deposit in significant amounts, the mass of alumina-silicates and other soil minerals dilute the concentration of Zr in the sediment.

That the model identifies Zr as associated with some risk may be due to using the conservative guideline values created in the context of radioactive anthropogenic Zr as other

knowledge is so limited (Shahid et al. 2013). Clearly, there is a need for research on Zr behaviour in the environment. However, until further research on Zr ecotoxicity is completed, it is suggested that the conservative approach be continued and accumulation of Zr in the environment be minimised.

4.1.14 Strontium

The priority ranking model ranked Sr from SP 28, TSP 32, blended 71, AP 127, piggery 135, poultry 136, cattle 146 and fish 190. Although these are relatively high rankings and Sr is not considered highly toxic to humans, concentrations in SP and RRP may be high enough to have environmental impacts on soil organisms (Appendix 2.11). Median Sr concentrations (Table 2.2) in SP (1070 mg kg^{-1}) and RRP (1420 mg kg^{-1}) were about 2 times guidelines for soil organisms (600 mg kg^{-1}, Appendix 2.11) and about 10 times the concentration in background soils (Table 2.2). Sr is not generally reported to have any biological function (Elias et al. 1982) but small quantities may be needed for the calcification of bones and teeth (D'Haese et al. 2000). Research on the toxicity of Sr has focused mainly on the effects of radioactive ^{90}Sr, which is an important constituent of nuclear fallout (Cabrera et al 1999). However, long-term ingestion of high concentrations of natural Sr causes "strontium rickets" in higher animals (Cabrera et al 1999) and has been associated with renal osteodystrophy (D'Haese et al. 2000). Sr acts as a proxy for Ca because both are alkaline earth elements with similar ionic radius and the same valence (Capo et al. 1998). Sr is believed to simply substitute for Ca (Elias et al. 1982), so it is ingested in similar ways to Ca. Because of this similarity it is also present in agricultural lime (Gabe & Rodella 1999) and can be concentrated in phosphorites, thus the levels found in mineral P fertilisers (Kabata-Pendias & Mukerjee 2007).

Recently however, Sr in drinking water has been identified as a potential health risk in Wisconsin, USA by researchers at the University of Wisconsin-Green Bay. In preliminary findings, 63% of water samples from municipal and private wells contained Sr levels higher than the Environmental Protection Agency's lifetime Health Advisory Limit of 4 mg L^{-1}, while 5% contained levels above 25 mg L^{-1}, which exceed the short-term exposure levels identified by the EPA. They concluded that children who drink the water for more than between one and 10 days

face an increased risk of developing health problems, including tooth enamel mottling and strontium rickets (Samson 2014).

Sources of Sr, other than fertilisers, include lime, ceramics, glass, industrial waste, combustion of coal and ash (Kabata-Pendias & Mukerjee 2007, Salminen et al. 2005).

Sr was predicted to be mobile (typical K_d 70-110, Appendix 2.8) and readily taken up by plants (typical TF 0.3-0.8, Appendix 2.9), consistent with the accepted scientific knowledge (Kabata-Pendias & Mukerjee 2007, Salminen et al., 2005). High CEC and pH, and low ionic strength increase Sr retention in soil but concentration in soil solution or groundwater is remains rarely solubility limited (Siegal & Bryan 2003). In acid soil, like those found in NZ, Sr is reported strongly leached down the profile (Salminen et al. 2005).

However, Sr accumulated in fertilised soils compared to non-fertilised soils (Figure 3.4). The only land use with significantly higher Sr was kiwifruit. Ca, and pH were also higher for these soils (pH 6.5, Appendix 1.2) suggesting a considerable quantity of lime, with Sr as a contaminant, has been applied. Addition of Ca to soil also decreases Sr phytoavailability (Kabata-Pendias & Mukerjee 2007).

The overall estimated application of Sr in SP in the top 10 cm of soil was 34.7 mg kg^{-1}, while the measured average accumulation of Sr was 26.9 mg kg^{-1} (Table 3.8). As, mixing by ploughing and soil organisms will increase the depth of soil impacted by Sr but dilute its concentration it appears nearly all the Sr applied in P fertiliser has been retained. However, additions of lime are also needed to maintain soil pH at optimum levels and these will add considerably to Sr applied. So it is likely that a proportion of Sr is unaccounted for.

Sr in the waters of Puketirini lake, a dune lake, were about twice the concentrations found in other lake and river waters (Table 3.10). Ca were also similarly higher. PCA of Waikato lake water showed Sr to be highly loaded on component 1 along with B, Ca, Mg, Mo, Na and U. PCA of Waikato River water and its tributaries showed Sr to be moderately loaded on component 2

along with Ca and Cu, and highly negatively loaded on component 4 along with B and Na. Sr is not currently measured in Regional Council groundwater monitoring samples.

In comparison, lake and estuarine sediments had clearly elevated median Sr concentrations (29-116 mg kg^{-1}) compared to those for natural background soil (16 mg kg^{-1}, Table 3.15). PCA of the lake and estuarine sediments showed Sr to highly loaded on the same components as Ca (Spearman's rank correlation r = 0.80 and 0.90 respectively). Consistent with Sr acting as a proxy for Ca, it appears likely that Sr in waters and sediments is following Ca and is controlled by the same mechanisms (Capo et al. 1998, Elias et al. 1982).

Although radionuclide ^{90}Sr is considered to be biologically hazardous for humans, there is no source of this radionuclide in nuclear-free NZ. Artificial radioactivity monitored in the environment in NZ has been measured at trace levels only, e.g. the average level for atmospherically deposited ^{90}Sr in 2000 was 0.2 Bq m^{-2} ± 0.2 (Tinker & Pilvio 2001)

These results are consistent with Sr being reasonably mobile with much of the Sr applied being transferred to sediment via water. However, concentrations in soils and sediments in NZ remain well below current guideline values so the environmental health consequences of Sr from fertilisers in these compartments are likely to be minor for the present. As monitoring of Sr in regional rivers has not been carried out, the impacts of Sr on the aquatic environment and on drinking water in NZ are yet to be established and consideration to such investigations should be given.

4.2 Fertiliser regime patterns among land uses in NZ

In all four fertiliser regimes tested fertilisers derived from P rock were used (Table 3.9). The assessment of fertiliser regimes showed impacts from all four regimes were remarkably similar, suggesting the type of fertiliser has little practical impact. It is likely the source of P rock has greater influence on the contaminant load of the finial fertiliser as concentrations of trace elements could vary considerably (Appendix 2.3). RRP is ground phosphate rock, so contaminants at source are carried through to the finished product. Superphosphate is derived through treating the rock with sulphuric acid – hence the useful sulphur component, but there

is limited opportunity to remove contaminants from the rock and again they remain in the product (Stacey et al. 2010). Triple Superphosphate, DAP and MAP are all manufactured with phosphoric acid. The nature of the phosphate rock used to produce the phosphoric acid will influence the levels of contaminants in the phosphoric acid, but by using different streams of phosphoric acid, lower contaminant levels are generally found in these products relative to sulphuric acid derived products. The third category includes the products derived with nitric acid, and these, generally, have a lower contaminant level (Gowariker et al. 2009).

No long-term sites trialling alternatives to P rock derived fertilisers in NZ were identified for comparison. Such a long-term field trial site needs to be developed in NZ.

4.3 How to manage contaminants found in fertilisers

4.3.1 Governance

A key challenge facing sustainable management of P fertilisers is that the costs of inefficient P use and losses of trace (and major) elements to the aquatic environment, including long-term and/or cross compartment environmental impacts, as these have not been adequately accounted for at the farm level. It is considered usually more effective to incentivise improvements in practice through education, subsidies and support for conservation practices than attempting to make the polluter pay (Jarvie et al. 2015, Shortle et al. 2012), although experience suggests both incentives and regulations are needed. Thus, good governance will encourage a best practice approach to managing contaminant build up in soils over the long-term through regulations and incentives. Proactive management to minimise the risk to health, land use flexibility and cross compartment environmental degradation should be considered. Such management would seek to prevent trace element losses to the environment and balancing of inputs to outputs, e.g. to reduce unwanted trace element contents input in fertilisers, only apply the amount of fertiliser nutrient needed. Experience and research shows many farmers apply far more fertiliser than they need for “insurance” (Jarvie et al. 2015).

An example for a load oriented type of management can be found in the German proposal of threshold values by the Ministries of Agriculture and Environment from 2002 known as “Good Quality and Secure Yields” (Gute Qualität und Sichere Erträge) (Bannick et al. 2006).

It was a response to the 2001 resolution of the German Ministries of Agriculture and Environment (Potsdam, June 13 2001), who declared that according to the precaution principle there must not be any long-term accumulation of harmful substances in the soil caused by cultivation practices such as fertilization. The ultimate goal was to sustain the current status quo of heavy metal concentrations on agricultural land. Accordingly, fertilising materials should not display heavy metal concentrations above those found on the land they were applied to, and a balance between heavy metal inputs from fertilisation and output (plant uptake) should be kept.

Dutch government departments are stimulating sustainable alternatives by the development of knowledge and information in cooperation with agricultural business. The Dutch organisation for entrepreneurs in agricultural and horticultural business (LTO) has recognised the trace element problem and is now willing to undertake activities to reduce the accumulation of heavy metals in agricultural soils (Schipper 2008). However, experience suggests broad recognition by farmers will take years of effort.

One useful tool could be open documentation as it allows the consumer to choose one brand over another, e.g. the amount of contaminants in fertilisers could be reported on the product packaging. A number of European countries, among them Austria, The Czech Republic, Denmark, Finland, Germany, Poland, Spain, and Sweden, have limited heavy metal contents in fertilisers by defining limit values in their national fertiliser regulations (some countries have limited only Cd, other countries, also limit elements such as As, Cu, Cr, Hg, Ni, Pb, Tl and Zn). However, a large proportion of the mineral fertilisers consumed in the European Union are EC (European Community) designated fertilisers, for which the national regulations do not apply (EC fertilises are estimated to 60-70% of the total consumption by CSES, 2010). While the estimated share of EC designated fertilisers in the total national consumption of mineral fertilisers is rather variable, ranging from less than 5% in countries like Denmark and Sweden up to more than 80% in Germany, Ireland or Spain. Therefore, the inclusion of heavy metal limit values into the EC Regulation 2003/2003 would prove much more effective than national regulations.

Monitoring of food products for standard exceedances, and identification of origin, is a powerful tool for public protection. However, there can be no protection if there is not a food standard (due to lack of information), e.g. no food standard is known for U, although there are guidelines for drinking water (WHO 2011).

4.3.2 Fertiliser Management

Achieving better P use efficiency by determining the most cost effective, efficient and appropriate fertiliser application and land management options reduce the amount of P fertiliser needed and contaminant trace elements applied. Options include greater recycling of P (in a clean form) in manure and in human and food waste, retaining P within the soil and increasing P availability for plant uptake (Jarvie et al. 2015). The appropriateness of options will vary depending on the type of land use, the size of operation, soil type, the need to protect vulnerable or special environments and other considerations, e.g. management of the environmental effects of Cd could be directed to minimising the occurrence of outwash (e.g. by better irrigation timing) or Cd transfer by using less Cd-rich phosphate fertiliser or minimising phosphate fertiliser use in areas susceptible to surface runoff (McDowell 2010).

The extraction of P from local waste products in a clean form, suitable and economical enough for use as fertiliser (Naidu et al 2012), is a fertile area of research. In the interim, it is good agricultural practice to minimise the amounts of contaminant trace elements input to farms in fertilisers.

Industry and government authorities in NZ have developed a strategy for managing Cd in fertilisers over the long term including a combination of governance, research, monitoring and management for food, soils and fertiliser (Cadmium Management Group 2011). Implementation of this strategy is likely to minimise contamination for several other mineral fertiliser-associated contaminants. The Cadmium Management Group recommends that to reduce Cd uptake into food crops phosphate fertilisers with low levels of Cd should be used, along with maintaining soil pH at the upper recommended limits for crop type and maintaining high SOM to reduce availability. It also recommends alleviating any Zn deficiency in the soil to avoid competition effects, minimising, and avoiding if possible, the

use of acidifying fertilisers as Cd is more mobile in acid conditions, and to avoid fertilisers and irrigation water containing high levels of Cl, which can form mobile Cd complexes.

4.3.3 Environmental Monitoring and Research

A well designed long-term monitoring programme will provide information on the ongoing status of trace elements in the soil environment; if they accumulate or are being lost to another part of the environment (e.g. ground or surface water), which will enable those involved directly (farmers etc) or indirectly (policy makers, governance) to assess and manage potential risks. Where there are knowledge gaps, such as a food standard for U, these need to be considered by researchers and funded by authorities.

4.3.4 Remediation

The best option is to simply not allow trace elements to accumulate to environmentally excessive levels. Unlike hydrocarbons, biodegradation into innocuous carbon dioxide and water is not possible for trace elements. Irrespective of soil chemical and biochemical reactions, the same metal will ultimately be present. Where accumulation does occur it is challenging to remediate due to the permanent, diffuse and widespread nature of the contamination, and the permanent nature of elemental contamination (elements do not break down except for radioactive decay, which still can result in a daughter contaminant).

Liming can be used to raise the pH and reduce the mobility of cations like Cd and Cu (Kabata-Pendias and Pendias 2001, Gray et al 1999). However, Ca in the lime can compete with cadmium for binding sites on the soil (Maurer et al 2012). Besides, liming does not remove the contaminants and they can become available again should the pH drop.

Deep ploughing can be used to dilute the contaminant within the soil profile. However, this does not remove the contaminant; but mixes it deeper into the soil and closer to groundwater.

Capping the contaminated soil with an impervious layer of clean material essentially removes trace element contaminants from contact with the rest of the environment. As rain water

cannot penetrate the cap there is no drainage and leaching of contaminants to groundwater. Similarly, plant roots cannot penetrate to reach the contaminants nor can the contaminants be resuspended as dust. However, this does not remove the contaminants and they can become available again should the cap fail.

Plants can be used to control contamination of a site and their use is one of the few remediation options that can remove contaminants. There are several plant related technologies including buffer zones (Uusi-Kamppa et al. 1996, Mander et al. 1996), phytomining (Nicks and Chambers 1994), phytoremediation, which is divided into phytoextraction and phytostabilization (Salt et al. 1995), as well as biofortification (King 2002). While biofortification is the improvement in trace element uptake by food or fodder crops, the other technologies may deliver a cost-effective means of mitigating environmental risks associated with a contaminated site (Robinson et al. 2009).

Planting buffer zones can reduce the amount of particle-born contaminants transferred to streams, rivers and lakes. Buffer zones removed 20-78% of total P (and presumably other particle-bound contaminants) in Finland (Uusi-Kamppa et al 1996) and wet meadows and grey alder forests in Estonia retained up to 12.8 kg P/ha/y (Mander et al 1996).

Phytoremediation may aim to immobilise contaminant trace elements in the soil, so that they neither leach nor enter the plant shoots (phytostabilization). Alternatively, one may engineer or manipulate the soil-plant system so that plants take up the contaminating trace elements into the shoots, where they may be volatilised (phytovolatilization), or removed from the site when the plants are harvested (phytoextraction). Phytomining describes the phytoextraction of valuable trace elements from metal-contaminated environments or ore bodies where the target metal concentration is too low for conventional mining. In soils that are deficient in essential trace elements, the goal of phytomanagement is to increase the trace element concentration in the edible plant organs (biofortification). The boundaries between these technologies are not distinct. Phytoextraction of trace elements from a contaminated soil may produce biomass enhanced in essential trace elements (biofortification) or saleable quantities

of valuable trace elements (phytomining), while reducing erosion and trace element leaching from the site (phytostabilization).

From a phytomanagement perspective, contaminated land can be utilised as a resource. Bioenergy and timber production on contaminated land has several advantages over production on non-contaminated fertile soils. Most importantly, productive agricultural land will not be taken out of food production, which, in the case of bioenergy production, has led to increased food costs (Economist 2007). Since the biomass produced either fixes carbon (timber) or produces CO_2-neutral energy (bioenergy), carbon credits may add further value to the operation. In addition to timber or bioenergy, the biomass of vegetation from a phytomanagement program may have other uses, where the possibly elevated concentrations of trace elements in the plant tissues are either unimportant (because they will not be consumed) or beneficial essential nutrients (such as selenium or zinc). This may include cut flowers, cotton, and stock fodder. In the latter case, the biomass may need to be monitored for excessive concentrations or the presence of other contaminants.

Phytomanagement is a long-term and site-dependent technology. It is only feasible if it satisfies environmental regulation and either returns a profit or costs less than alternative technologies or inaction.

When groundwater is contaminated with metals, remediation alternatives are limited to mobilisation or immobilisation. Generally, it is easier to immobilise a metal than it is to mobilise and recover it. However, an immobilised metal may still be a source of future problems if subsurface ambient conditions change (Vance 1994). Mobilisation and pumping is limited to highly polluted situations and is not suitable for low-level, diffuse contamination (Uusi-Kamppa et al 1996).

4.3.5 Recommendations for further research

Raw materials low in contaminants. Nations now realise the value of more pure resources and restrict sale of such low-contaminant material (Herring & Fantel 1993), e.g. low contaminant containing P rock. Manures and low–metal waste streams should be considered

as potential fertiliser sources. Appendix 2.3 and Table 2.2 showed that contaminant levels were lower for fertilisers made from cattle, plant and some fish products than those for conventional mineral fertilisers. There should be more emphasis on the extraction of P from local waste products in a clean form, suitable and economical enough for farm use (Naidu et al 2012), such as struvite.

Removing contaminants during processing. Some techniques for removing contaminants are currently available but are not considered economic and research into improving the economic viability of these is warranted, e.g. F is released from P rock as gaseous F during the acidification process and the gases are removed by scrubbers. However, scrubber effluent is often used in the granulation process for SP in NZ, which results in all the F in the raw P rock ending up in the fertiliser (Loganathan et al. 2003). It would be relatively simple to trap the F in the scrubber effluent and dispose to a controlled landfill; wet chemistry techniques can remove several contaminants from mineral P fertilisers, e.g. Pb can be precipitated as the salt of sulphate; in acidic water, F can be removed by adding lime to pH 3 to precipitate most of the F as CaF_2 (Ando & Hamada 1994, Górecki 1994); U has been extracted from phosphate in the past for nuclear fuel.

Minimising leaching or runoff by overland flow. Practices that minimise leaching or overland flow of water are commonly used in NZ to manage nutrient and sediment loss. These practices also have the benefit of minimising the loss of contaminants, e.g. maximising efficiency of irrigation water; planting riparian zones, buffer strips or filter strips of dense vegetation to impede run-off and help filter contaminants and sediment; using conservation tillage and crop rotation techniques. Research should focus on both improving the effectiveness of these practices and the uptake by industry.

Nutrient management. A comprehensive nutrient management plan is useful to determine the proper fertiliser application rates. Yearly soil sampling is used to determine plant needs and to make accurate fertiliser recommendations. Also fertiliser can be applied accurately using precision agriculture techniques (Figure 4.9). Research should focus on both improving the effectiveness of nutrient management and the uptake by industry.

Figure 4.9: Farm tractor equipped with precision agriculture apparatus (Landwise Incorporated).

Developing of risk-based guidelines to protect the environment

Lack of ecotoxicity data is limiting the accuracy and the quality of many currently available guidelines, therefore, the ability to provide guidance for environmental management, e.g. ecotoixicty data for F and U generally, and for B in the brackish environment.

Other investigations:

- The contribution of fertiliser enhanced soil weathering of soil minerals to soil formation is poorly understood and requires quantification.
- The interactions between fertilisers and algae blooms including trace element seeding of such blooms (where a trace element is a limiting nutrient) may be important, while the bloom induced increase in water pH that releases elements into the water column appears to have not been previously reported.
- The behaviour and environmental impact of several elements is poorly understood in some parts of the environment. These elements include the behaviour of Ag lost from fertilised soils (including kinetic studies), Ag and B in the brackish environment, and the REE and Zr, including identification and quantification of any other sources apart from fertiliser.
- Comprehensive mass balance modelling for trace elements in soil including quantifying soil – plant interactions and soil – water interactions reqired underpinning studies

5 Conclusions

The information presented in this thesis may provide technical support for policy makers, resource managers and researchers to guide decision making and allocation of priorities. In NZ, this includes regional authorities carrying out analysis under the RMA and implementation of policy methods responding to the diffuse contamination associated with the use of fertilisers. Contaminants in fertilisers have the potential to accumulate or be transported across environmental boundaries. Research to reduce adverse impacts of fertiliser associated trace elements should be considered. Such research could focus on preventing contaminants getting into fertiliser, using raw materials with low levels of contaminants, and using best management practices for nutrient management in agriculture and horticulture. Consideration should be given to expanding the Fertmark Quality Assurance Scheme, analogous to limit values for Cd, to include maximum limits for other contaminants in both mineral and organic fertilisers. Each additional contaminant will need research to underpin any maximum limit.

The results of the PCA of soil and assessing soils by land use or the simplified soils data (placed in fertilised or unfertilised categories) showed accumulation of most contaminant elements predicted to accumulate from additions of inorganic P fertiliser and organic alternative fertilisers, e.g. Cd, P, U, F, La and Zn.

The elements predicted to be highly mobile did not accumulate in soil, despite considerable amounts of some of these elements being applied in fertiliser, e.g. B.

The soil environment is not constant and several factors, including pH and redox, can affect the mobility of trace elements currently accumulated on soils or sediment. The addition of fertiliser enhances soil weathering processes and this process requires further research.

The quantitative ranking model results showed there was a prevalence of trace elements from conventional inorganic P fertilisers in the top 25 ranks. While Cd, F and U were anticipated, the high ranking for B was unexpected. Zn, Cu, Sr, La and Zr also ranked in the top 30.

Investigating fertiliser regime patterns found SP was by far the most popular fertiliser applied in NZ. However, RRP was used by organic farmers and soils receiving this fertiliser had the highest median concentrations for acid extractable P, Cd, and Sr.

Accumulation of the known mineral P fertiliser associated elements Cd, F and U in estuarine sediments was not apparent. There was also no relationship between fertiliser use and F in fresh water lake sediments. There was no clear evidence of fertiliser–F enhancement in groundwater, although this could not be excluded. F added to soil in fertiliser appears fully retained by the soil. On the other hand, Cd and U were elevated in some of the fresh water lake sediments, especially those surrounded by intensively farmed land uses. This result suggests some Cd and U were transported to lakes as particles that settle to form sediment or in a dissolved form that was sorbed onto existing lake sediment.

There were increases in concentrations of some elements in shallow lake waters associated with algal blooms. Algal blooms impact water pH by increasing it. The increased water pH appears to result in the release of certain elements into the water column, e.g. B, Mo, U and V. This phenomenon should be further investigated.

Levels of Cd and U were below detection limits in the Waikato River samples, possibly due to dilution. Monitoring of groundwater bores showed Cd was detected in just 15% of the samples, but these samples tend to be from high intensity farming areas. However, the maximum level was still only ½ the drinking water standard for NZ and well below the trigger value for freshwater protection for 95% of species.

No long-term sites receiving alternatives to P rock derived fertilisers were identified for comparison. Consideration should be given to developing such a long-term field trial site in NZ.

There were specific impacts from the different trace elements that need considering:

- The accumulation of F in soil is likely to increase F uptake by livestock with ingestion of soil containing high concentrations of F potentially leading to chronic fluorosis in

stock. Excessive F has been shown to negatively impact soil microorganisms, aquatic organisms and plants. Research into risk-based guidelines to manage the risks to animals and ecosystem receptors, and to producing low-F fertilisers to reduce the rate of F accumulation in NZ soils should be carried out.

- In NZ, U is accumulated in soil or effectively trapped in the lake sediments and is not progressing further down the rivers to the estuarine environment. The effect of this accumulation on lake and soil organisms is unknown and consideration should be given to undertaking ecotoxicity studies to provide guidance for environmental management.
- Consideration should be given for research to establish a NZ risk-based soil guideline value for U to protect the environment and human health. Until such a guideline is derived, a conservative approach could be followed in land management because of the chemical and radiotoxicity of U and our lack of knowledge of safe levels in soil.
- Cd significantly accumulated in NZ soils under all the fertilised land uses assessed in this study. Cd accumulation in soil can be minimised if the concentration of cadmium in the applied phosphate product is low, e.g. less than 5 mg kg^{-1}.
- Ag is an emerging contaminant as Ag nanoparticles are increasingly used as a bactericide and virucide, thus constitute a new risk in the environment, especially if they finish up in organic materials that can be used as fertilisers. Consideration should be given to further investigations, with the development of guidelines and procedures to prevent Ag contamination becoming a significant environmental contaminant in fertilisers. The enhanced levels of Ag in estuarine sediments suggest some Ag may transfer from soil. Ag is not currently measured in NZ Regional Council surface water or groundwater monitoring samples but such monitoring may be justified to underpin regulations if these are required.
- B is highly mobile and being depleted from soils, despite large additions in fertilisers and other products. B is accumulating in saline estuarine sediments. However, there appears little understanding of the potential effects to the estuarine environment, such as to sediment microorganisms, shellfish, aquatic plants and seaweeds. The change from a low B environment to one where B is abundant or even toxic, has considerable implications for New Zealand's aquaculture industry and requires further study.

Studies to identify and quantify the source of B accumulation in the estuarine environment should be considered (e.g. fertiliser, timber treatment chemicals, powder coatings) so that suitable controls can be developed.

- The limited soil information in this study did not support Zr accumulation in soil being a major issue in NZ. That the model identified Zr as at some risk may be due to using the conservative guideline values associated with radioactive anthropogenic Zr as knowledge of natural Zr is limited. However, until further research on Zr ecotoxicity is completed, it is suggested that the conservative approach be continued and accumulation of Zr in the environment be minimised.
- There was relatively little ecotoxicity data for REE, which makes justifying guidelines problematic. Until further research is completed, it is suggested that a conservative approach be adopted and accumulation of REE in the environment be minimised.

6 Summary/ Zusammenfassung

The main objective of the present research work was a systematic evaluation of the range and quantity of elemental contaminants applied to land in fertilisers and their wider environmental impacts. The retrospective assessment of a wide range of anthropogenic fertiliser associated contaminants across a representative range of natural and productive land uses, and soil orders in New Zealand (NZ) receiving real-world inputs of fertiliser, and their transfer across environmental compartments was carried out. A systematic and transparent prioritisation methodology to model the consequences to the environment and to human wellbeing from the application of trace elements was presented to help identify where issues may arise in the future and what issues were of greatest precedence. Trace elements applied to soil in organic fertilisers as well as those found in inorganic mineral P fertilisers were assessed. The modelled results were validated against a synthesis of a large soil monitoring dataset and smaller groundwater, river and stream, lake and estuarine sediment datasets. Most of the data were from the Waikato region. Such resulting rankings and the underpinning information can be used by policy makers, resource managers and researchers to guide decision making and allocation of priorities.

The main findings were:

No single fertiliser group was free of all contaminants. Ag, B, Cd, F, REE, Sr, and U in mineral fertilisers and Cu and Zn in fertilisers made from manures and other organic materials were the elements most elevated compared to concentrations found in background soils.

Testing the results of the model against a large soil monitoring dataset confirmed the model provided accurate assessments of the environmental risks of elemental contaminants. Elements predicted to accumulate from additions of inorganic P fertiliser and alternative organic fertilisers (e.g. Cd, P, U, F, La, Zn) were elevated in fertilised soils compared to background soils. Elements predicted to be highly mobile generally did not show accumulation in soil, despite considerable amounts being applied in fertiliser, e.g. boron (B).

Many of the elements in water samples appeared associated with land use, e.g. low concentrations of B, Ca, and K a were lowest in stream and river water samples from native forest land use catchments and higher in land used for forestry and pasture. Monitoring of groundwater bores showed Cd was detected in just 15% of the samples, but these samples tend to be from high intensity farming areas. However, the maximum level was still only ½ the drinking water standard for NZ and well below the trigger value for freshwater protection for 95% of species. Data for three lakes affected by algal blooms showed water pH increased to >8.5 which may be causing dramatic changes in solution chemistry leading to the release of certain elements into the water column, e.g. Mo, U, V. These occurrences require further research.

No relationship was found between fertiliser use and F or U in fresh water lake sediments and F and U added to soil in fertiliser appeared to be fully retained by the soil. On the other hand, P, Cd, Cu, Ag and Zn were elevated in some of the fresh water lake sediments, especially those surrounded by intensively farmed land uses, consistent with fertiliser being a source.

This study identified specific impacts from the different trace elements in the NZ environment. These were:
F accumulated in the soil with soil ingestion the most likely mechanism for ingestion of F by animals. There was a lack of risk-based guidelines to direct research on the management of the impacts of F to animals and ecosystem receptors.

U accumulated in soil or was effectively trapped in the lake sediments. Like for F, there was a lack of risk-based guidelines to direct research on the management of the impacts of U to animals and ecosystem receptors. Not only do fertiliser additions apply U to soil, but they also increase the availability of native, recalcitrant U through enhanced weathering of soil minerals. The mechanisms of this enhanced weathering phenomenon should be further studied.

Cd had significantly accumulated in NZ soils under all the fertilised land uses assessed in this study. A proportion of the added Cd was not held on the soil and may be taken up by plants or leached to water and to sediments.

Ag levels in some fertilisers were higher than expected and Ag may be an emerging contaminant in fertilisers. Results suggested little Ag has been applied to NZ soils thus far, while the enhanced levels of Ag in estuarine sediments suggest Ag may transfer from soil to estuaries. Therefore, a watching brief should be kept on this element by researchers to better identify transfer and accumulation mechanisms, as well as any environmental risks.

B was highly mobile in soils, which were receiving considerable B additions from fertilisers and other products but accumulated in saline estuarine sediments. This process and it implications for life within the brackish environment appears poorly understood and should be further studied.

No long-term fertiliser trial sites receiving alternatives to traditional mineral fertilisers were identified in NZ. Consideration should be given to the development of such long-term field trials to compare with conventional fertiliser trials.

It is suggested that research should be conducted into expanding the Fertmark Quality Assurance Scheme, analogous to limit values for Cd, to include maximum limits for other contaminants in both mineral and organic fertilisers.

Zusammenfassung

Hauptanliegen dieser Forschungsarbeit war eine systematische Bewertung der Mengen an anorganischen Schadelementen, die mit Düngemitteln in die Fläche gelangen, sowie deren Auswirkungen auf die Umwelt. Es wurde eine retrospektive Betrachtung einer großen Anzahl düngergebundener anthropogener Schadstoffe über eine repräsentative Auswahl mit Düngemitteln versorgter natürlicher und produktiver Landnutzungstypen und Bodentypen in Neuseeland durchgeführt. Um die Konsequenzen der Zufuhr von Spurenelementen für die

Umwelt und die menschliche Gesundheit zu modellieren wurde eine systematische und transparente Priorisierungsmethode eingesetzt, die dazu diente, künftig zu erwartende Probleme und vorrangig zu lösende Aufgaben zu identifizieren. Bewertet wurden sowohl Spurenelemente in organischen als auch solche in anorganischen (mineralischen) Düngemitteln. Die modellierten Ergebnisse wurden mithilfe eines umfangreichen Bodenmonitoringdatensatzes sowie mehrerer kleinerer Datensätze zu Grundwasser, Flüssen und Strömen, Seen und Wattsedimenten validiert. Ein Großteil der Daten stammen aus der Waikato Region. Somit lassen sich die resultierenden Ergebnisse zusammen mit der dazugehörigen Hintergrundinformation von Politikern, Ressourcenmanagern und Wissenschaftlern als Hilfestellung bei der Entscheidungsfindung und Prioritätensetzung nutzen.

Die Studie erbrachte folgende Ergebnisse:

Keine der betrachteten Düngemittelgruppen war frei von jeglichen Schadstoffen. In mineralischen Düngern waren im Vergleich zu Hintergrundgehalten in Böden vor allem die Konzentrationen an Ag, B, Cd, F, REE, Sr und U stark erhöht, während in Wirtschaftsdüngern und anderen organischen Düngemitteln insbesondere Cu und Zn hohe Konzentrationen aufwiesen.

Die Validierung der Ergebnisse anhand des Bodenmonitoringdatensatzes bestätigte, dass das Modell eine präzise Einschätzung der Umweltrisiken anorganischer Schadelemente liefert. Diejenigen Elemente, für die das Modell eine Anreicherung aufgrund von mineralischer P-Düngung bzw. organischer Düngung vorhersagte (z.B. Cd, P, U, F, La, Zn), waren in gedüngten Böden im Vergleich zu Hintergrundböden tatsächlich erhöht. Elemente, denen eine hohe Mobilität zugeschrieben wurde, zeigten generell keine Anreicherung im Boden, auch dann nicht, wenn sie mit der Düngung in hohen Mengen zugeführt wurden, z.B. Bor.

Viele der in den Wasserproben gemessenen Elemente zeigten einen Zusammenhang mit der Landnutzung, so waren beispielsweise die Konzentrationen von B, Ca und K in denjenigen Proben am niedrigsten, die aus mit natürlichem Wald bestandenen Einzugsgebieten stammten, während Proben von Flächen unter waldwirtschaftlicher oder Weidenutzung höhere Gehalte dieser Elemente aufwiesen. Von den aus dem Grundwassermonitoring stammenden Proben zeigten nur 15% messbare Cd-Gehalte, wobei diese überwiegend aus Regionen mit intensiver Landwirtschaft kamen. Der höchste gemessene Gehalt betrug allerdings nur die Hälfte des

Trinkwasserstandards für Neuseeland und lag damit deutlich unterhalb des sog. „Trigger Values“ (= Prüfwert) zum Schutz von Frischwasserreserven für 95% der Arten. Drei von Algenblüte betroffene Seen zeigten Anstiege im Wasser-pH auf Werte >8,5, wodurch dramatische Veränderungen in der Lösungschemie hervorgerufen werden können, die sich z.B. in der Freisetzung einiger Elemente wie Mo, U und V in die Wassersäule zeigen. Diese Beobachtungen erfordern eine weitergehende Untersuchung.

Zwischen dem Düngemitteleinsatz und den Gehalten an F und U in Frischwasserseesedimenten wurde keine Beziehung gefunden, das mit der Düngung eingetragene F und U scheinen vollständig vom Boden zurückgehalten zu werden. Andererseits waren die Gehalte an P, Cd, Cu, Ag und Zn in einigen der Frischwasserseesedimentproben erhöht, insbesondere dort, wo die Seen von intensiv genutztem Farmland umgeben waren. Dies untermauert die Annahme, dass als Quelle der Elementgehalte Dünger in Betracht kommen.

Die vorliegende Studie identifizierte spezifische Auswirkungen der unterschiedlichen Spurenelemente für die Umwelt Neuseelands. Diese waren wie folgt:

F-Anreicherung im Boden bzw. die Aufnahme von Boden durch Weidetiere ist als wahrscheinlichster Mechanismus für die Aufnahme von Fluor durch Weidetiere zu sehen. Hier gab es einen Mangel an risikobasierten Richtlinien, die der Forschung zum Management der Auswirkungen von F auf Tiere und Ökosystemrezeptoren einen Weg weisen könnten.

U reicherte sich im Boden an bzw. wurde effektiv in Seesedimenten zurückgehalten. Wie bei Fluor gab es auch bezüglich U einen Mangel an risikobasierten Richtlinien, die der Forschung zum Management der Auswirkungen von U auf Tiere und Ökosystemrezeptoren einen Weg weisen könnten. Düngung trägt nicht nur Uran in den Boden ein, sondern sie erhöht auch die Verfügbarkeit von nativem, persistentem Uran, da sie die Verwitterung von Bodenmineralen fördert. Die diesem Phänomen der verstärkten Verwitterung zugrunde liegenden Mechanismen sollten genauer untersucht werden.

Cd war in allen gedüngten Landnutzungsvarianten der vorliegenden Studie im Boden angereichert. Ein Teil des zugeführten Cadmiums wurde nicht vom Boden zurückgehalten und war so der Pflanzenaufnahme bzw. der Auswaschung ins Wasser und in Sedimente zugänglich.

Ag-Gehalte waren in einigen Düngertypen unerwartet hoch und stellen möglicherweise einen neu zutage tretenden Schadstoff in Düngemitteln dar. Die hier gewonnenen Ergebnisse lassen annehmen, dass bisher wenig Ag auf neuseeländischen Böden eingetragen wurde, während die erhöhten Ag-Gehalte in Wattsedimenten nahe legen, dass Ag vom Boden in die Flussmündungen transferiert wird. Daher sollte dieses Element weiterhin durch die Forschung beobachtet werden, um Transfer- und Akkumulationsmechanismen sowie Risiken für die Umwelt besser identifizieren zu können.

B war hoch mobil in solchen Böden, die bedeutende Mengen an B-Zufuhr durch Dünger und andere Produkte erhielten, jedoch akkumulierte es in salzreichen Wattsedimenten. Dieser Prozess ebenso wie seine Implikationen für das Leben im Brackwasserregime sind bisher nur unvollständig verstanden und sollten weiter untersucht werden.

In Neuseeland konnten keine Langzeitversuchsflächen gefunden werden, die dem Vergleich von alternativen Düngemitteln mit herkömmlichen mineralischen Düngern gewidmet sind. Es wäre zu überlegen, solche Langzeitversuche einzurichten, um derartige Vergleiche durchführen zu können.

Es wird vorgeschlagen, dass die Forschung sich einer Ausweitung des sog. „Fertmark Quality Assurance Systems“ (= Qualitätssicherungssystem) widmet, welches neben Grenzwerten für Cd auch solche für weitere elementare Schadstoffe in mineralischen und organischen Düngern enthalten sollte.

6 Acknowledgements

I would like to firstly acknowledge my supervisor Prof. Dr. Dr. habil. Dr. h.c. Ewald Schnug for his encouragement, wisdom and support. This project would not have happened without him.

Liston, my sons, to a father's instruction;
pay attention and gain understanding.
I give you sound learning,
so not forsake my teaching.

Proverbs 4: 1-2

I also acknowledge the support of my regional council colleagues and the following regional councils which supplied monitoring data used to verify the model: Auckland Council, Waikato Regional Council, Bay of Plenty Regional Council, Taranaki Regional Council, Greater Wellington Regional Council, Tasman District Council and Marlborough District Council.

I am also very thankful to all my colleagues of the Institut für Pflanzenbau und Bodenkunde, JKI for making me welcome every time I visit. I particularly want to acknowledge Dr. Sylvia Kratz and Dr. Judith Schick for their editing of my thesis and our many discussions over tea, and Prof. Dr. Silvia Haneklaus for allowing me to stay at her flat while I was in Germany.

Thanks also to Peter Hardi for help with the SEM and EDAX, Dr. Geerd Smidt, who strongly encouraged me to start this PhD journey, and to Dr. Nick Kim, who has been my co-worker on many related studies.

Finally, my thanks to my wife Jo, who put up with me through the stresses and strains.

A good woman is hard to find,
and worth far more than diamonds.

Proverbs 31: 10

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